PROPERTIES OF POLYMERS

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Introduction

- Different properties of polymers such as,

  PHYSICAL, THERMAL, AND MECHANICAL

- **Physical properties:** polymers include molecular weight, molar volume, density, degree of polymerization, crystallinity of material, and so on..

- **Thermal properties:** melting point and glass transition temperature.

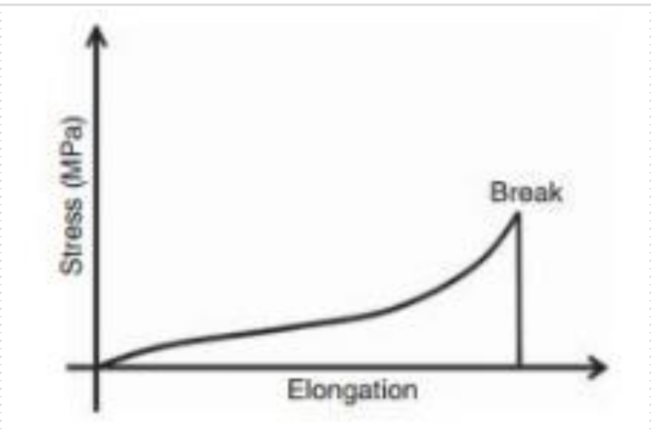
- **Mechanical properties:** strength, elongation, young's modulus, toughness, viscoelasticity

Mechanical Properties

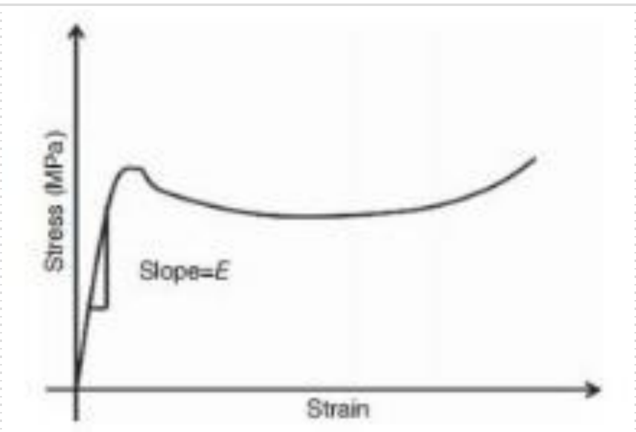
- some basic mechanical properties of the polymer material before its application in any field, such as how much it can be stretched, how much it can be bent, how hard or soft it is, how it behaves on the application of repeated load and so on
- ***Strength****:* In simple words, the strength is the stress required to break the sample. There are several types of the strength, namely tensile (stretching of the polymer), compressional (compressing the polymer), flexural (bending of the polymer), torsional (twisting of the polymer), impact (hammering) and so on.
- The polymers follow the following order of increasing strength: linear < branched < cross-linked < network.
- ***Factors Affecting the Strength of Polymers*****:** Molecular weight, cross-linking, and crystallinity.

- ***Percent Elongation to Break (Ultimate Elongation):*** It is the strain in the material on its breakage, as shown in (Fig 1). It measures the percentage change in the length of the material before fracture. It is a measure of ductility. Ceramics have very low (<1%), metals have moderate (1–50%) and thermoplastic (>100%), thermosets (<5%) value of elongation to break.
- ***Young's Modulus (Modulus of Elasticity or Tensile Modulus):*** Young's Modulus is the ratio of stress to the strain in the linearly elastic region (Fig 2). Elastic modulus is a measure of the stiffness of the material.

  E = Tensile Stress (σ) / Tensile Strain(ε)



Elongation to break of the polymer Fig 1



Young's modulus of the polymer Fig 2

Stress-Strain behavior of polymers

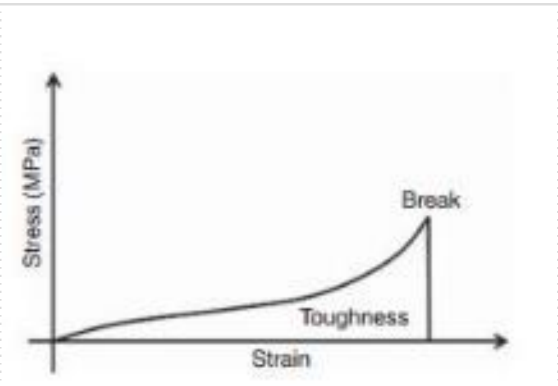
- ***Toughness:*** The toughness of a material is given by the *area under a stress–strain curve* (Fig 1).

  Toughness = $\int \sigma \, d\varepsilon$

- A typical stress–strain curve is shown in (Fig 2), which compares the stress–strain behavior of different types of polymeric materials.

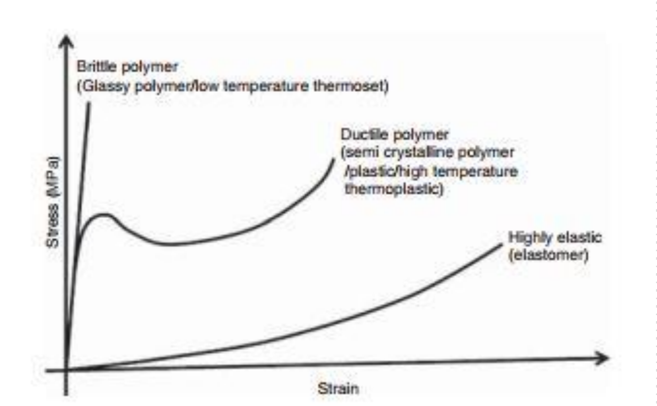
- The rigid materials possess high Young's modulus (such as brittle polymers), and ductile polymers also possess similar elastic modulus, but with higher fracture toughness. However, elastomers have low values of Young's modulus and are rubbery in nature.

Fig 1



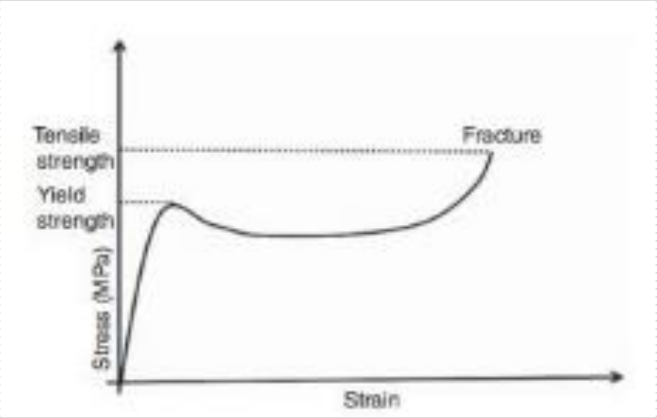
The toughness of polymer material

Fig 2

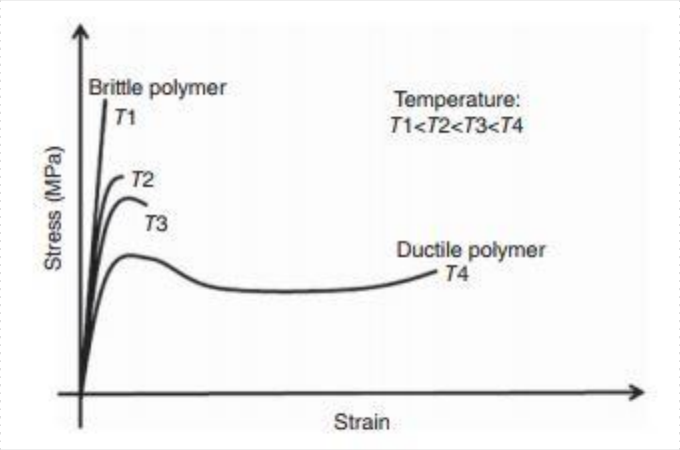


Stress–strain behavior of different types of materials.

- The yield strength of the plastic polymer is the corresponding stress where the elastic region (linear portion of the curve) ends (Fig.1). The tensile strength is the stress corresponding to the fracture of the polymer. The tensile strength may be higher or lower than the yield strength (Fig.1).
- The mechanical properties of the polymer are strongly affected by the temperature. A typical plot of stress versus strain is shown in (Fig.2). From the plot, it is clear that with increase in the temperature, the elastic modulus and tensile strength are decreased, but the ductility is enhanced



Yield strength and tensile strength of polymer. Fig. 1



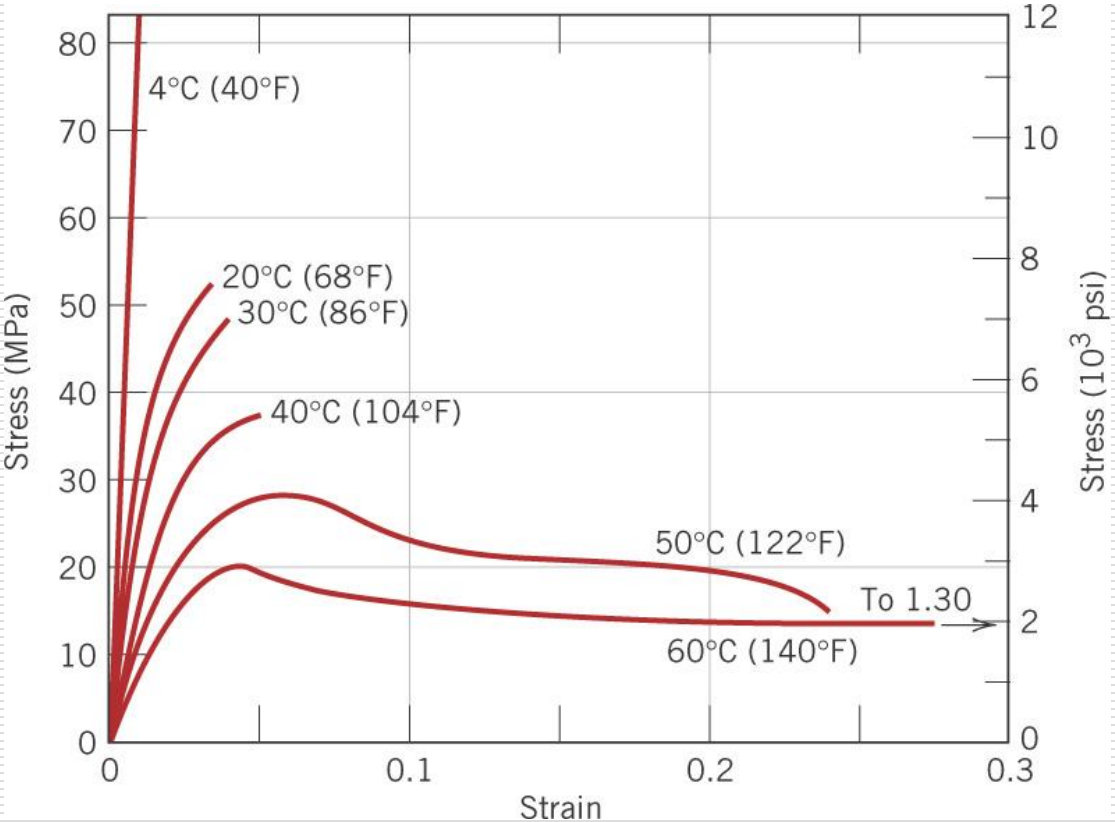
Effect of temperature on the mechanical properties of polymer. Fig. 2

Temperature & Strain Rate:Thermo-Plastics

The influence of temperature on the stress–strain characteristics of poly(methyl methacrylate).

- **Decreasing T...**
  --increases E
  --increases TS
  --decreases %EL

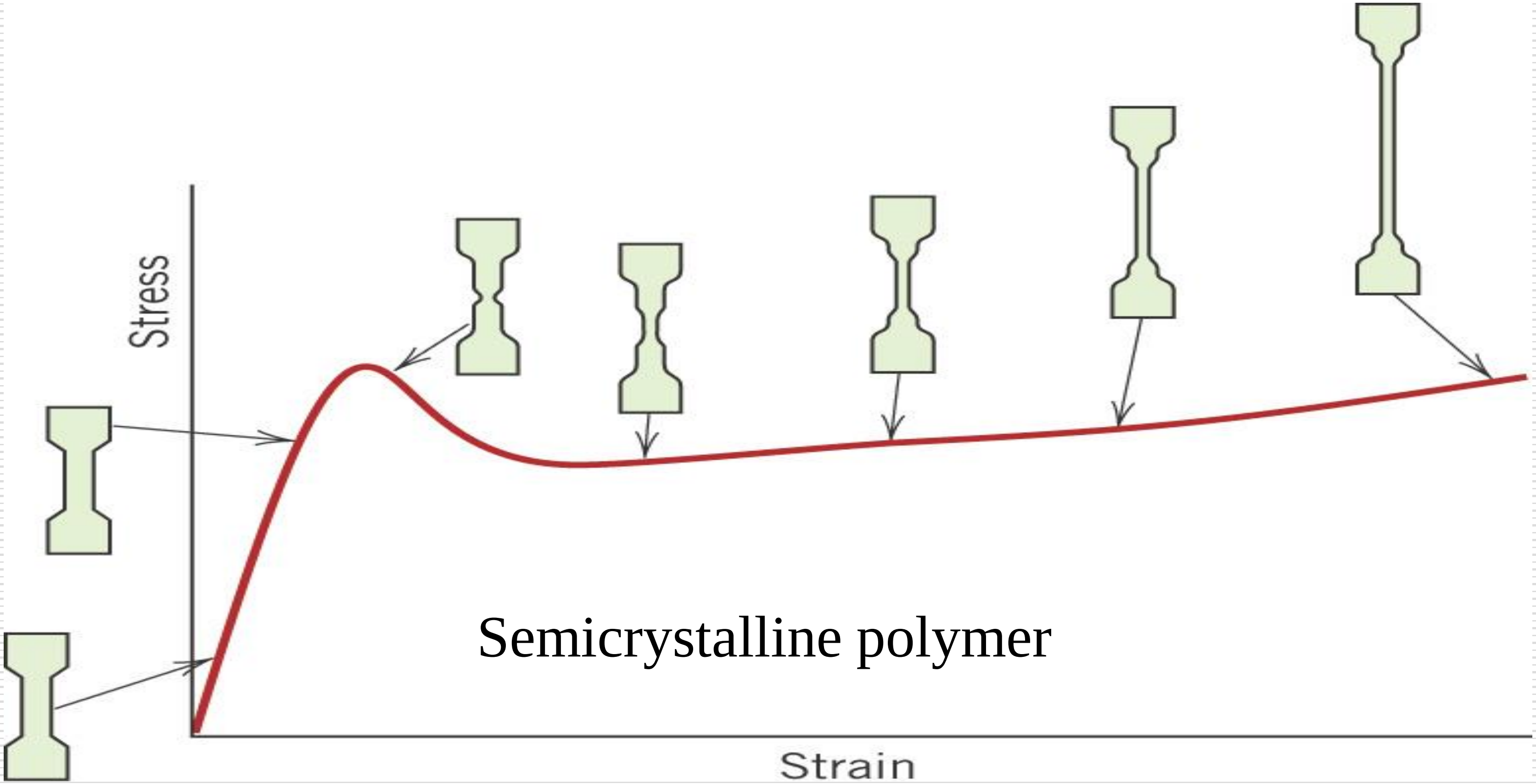
- **Increasing strain rate...**
  --same effects as decreasing T.



Ref.- T. S. Carswell and H. K. Nason, "Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics," Symposium on Plastics, American Society for Testing and Materials, Philadelphia, 1944.

Macroscopic Deformation

Schematic tensile stress–strain curve for a semicrystalline polymer.



Ref.- Jerold M. Schultz, Polymer Materials Science, copyright © 1974, p. 488. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ

Visco-elasctic deformation

- ***Viscoelasticity**:* There are two types of deformations: elastic and viscous. Consider the constant stress level applied to a material.
- Usually, polymers show a combined behavior of elastic and plastic deformation (Fig.) depending on the temperature and strain rate.
- At low temperature and high strain rate, elastic behavior is observed
- At high temperature but low strain rate, the viscous behavior is observed.
- The combined behavior of viscosity and elasticity is observed at intermediate temperature and strain rate values. This behavior is termed as *viscoelasticity,* and the polymer is termed as *viscoelastic*.

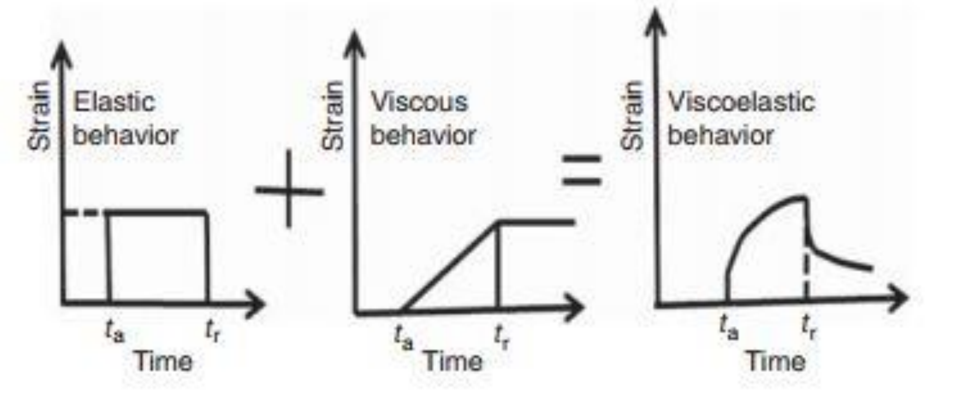
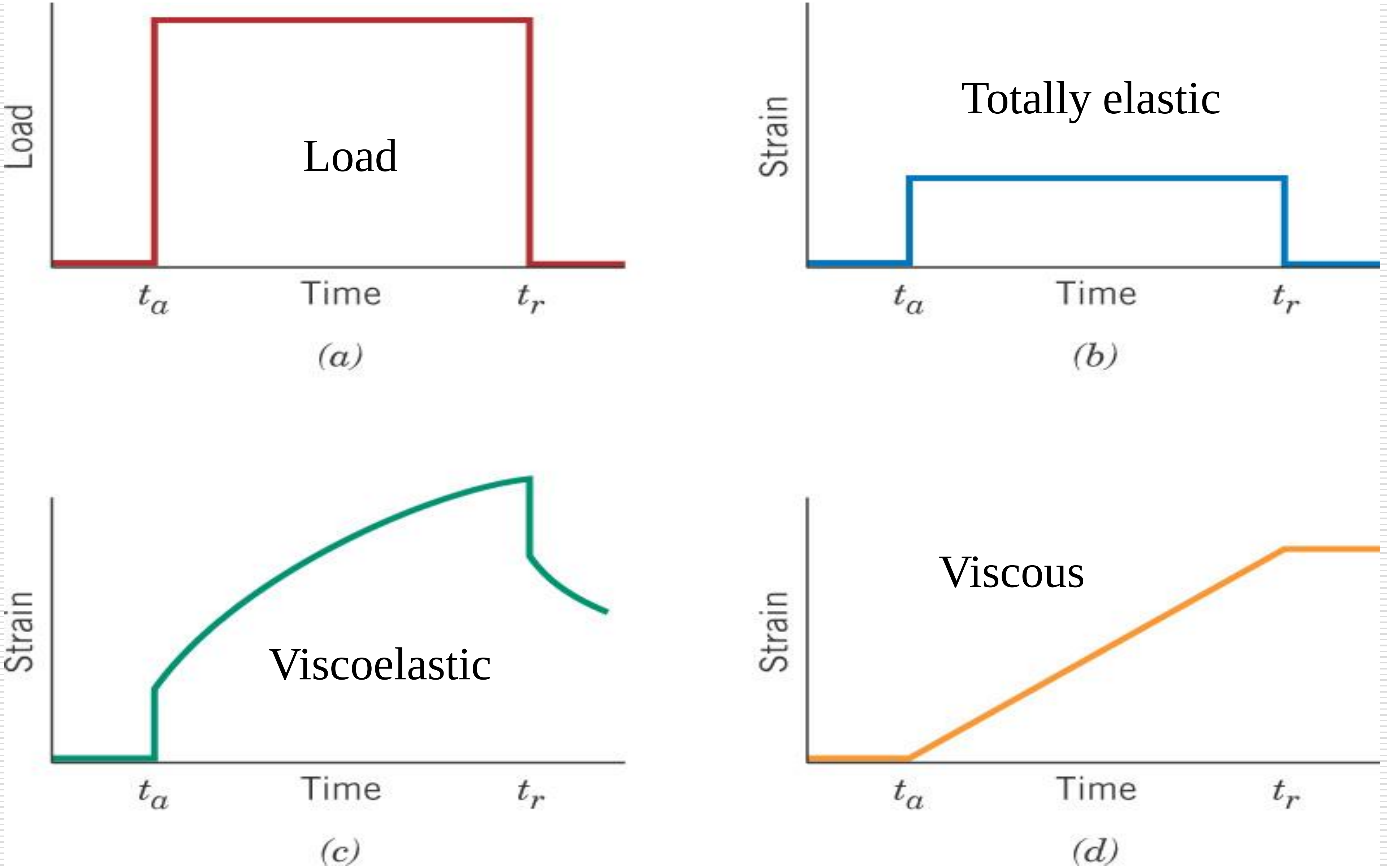


Fig: Viscoelastic deformation: the combined behavior of viscosity and elasticity.


Load
Load
t_a
Time
t_r
(a)
Strain
Totally elastic
t_a
Time
t_r
(b)
Strain
Viscoelastic
t_a
Time
t_r
(c)
Strain
Viscous
t_a
Time
t_r
(d)

Relaxation Modulus for Visco-eleastic Polymers

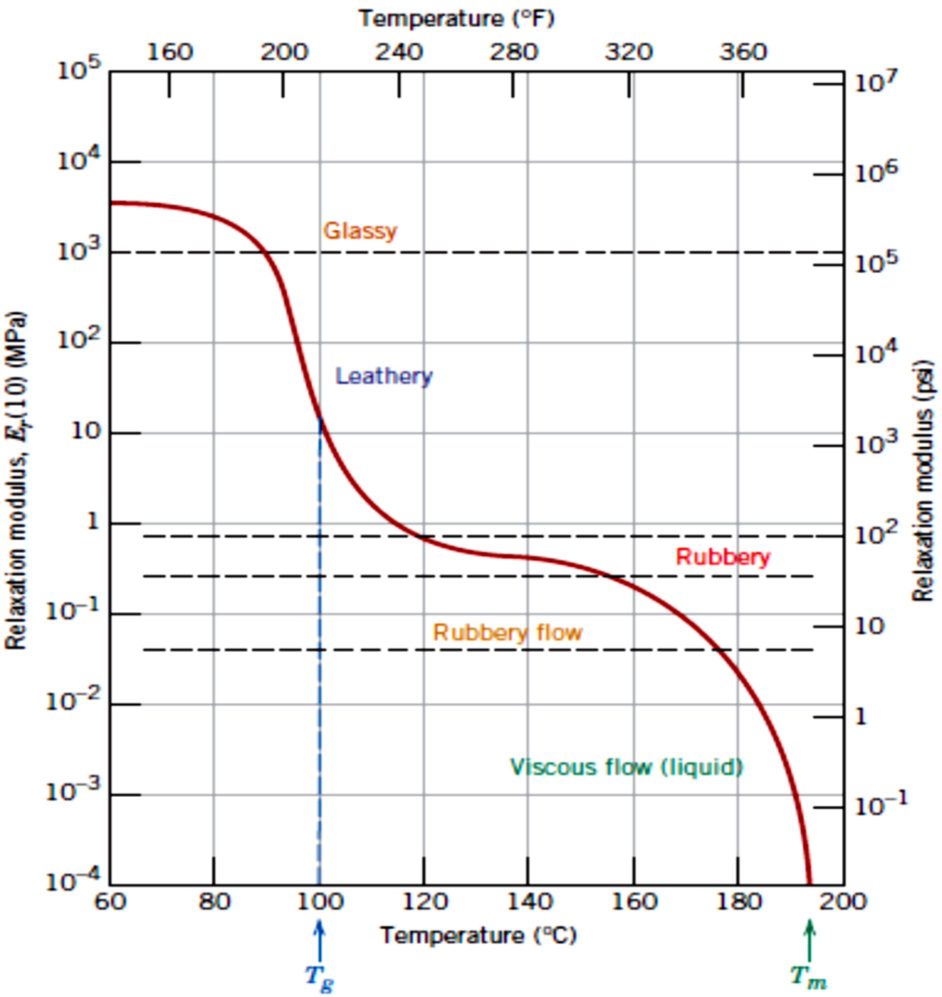
We may define a relaxation modulus *Er(t)*, a time-dependent elastic modulus for viscoelastic polymers

$$E_r(t) = \frac{\sigma(t)}{\varepsilon_o}$$

Where,

$\sigma(t)$ is the measured time-dependent stress

ε_0 is the strain level, which is constant



Ref.- A. V. Tobolsky, Properties and Structures of Polymers. Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

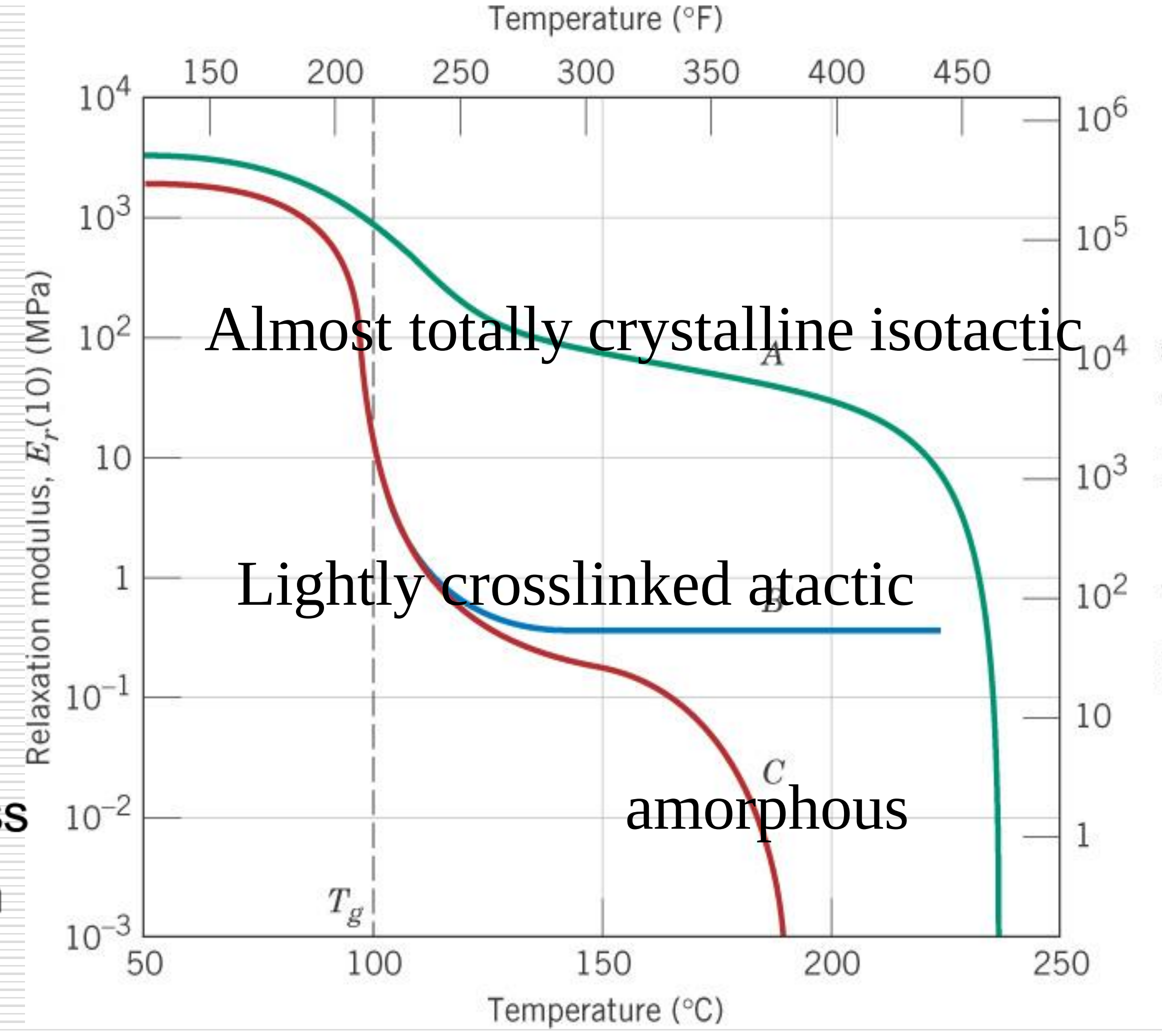
Polystyrene Configuration

Many polymeric materials are susceptible to time-dependent deformation when the stress level is maintained constant; such deformation is termed *viscoelastic creep*.

$$E_c(t) = \frac{\sigma_o}{\varepsilon(t)}$$

σ_o is the const. applied stress

$\varepsilon(t)$ is time-dependent strain



Ref.- A. V. Tobolsky, Properties and Structures of Polymers. Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc

Other Mechanical Properties

IMPACT STRENGTH:-

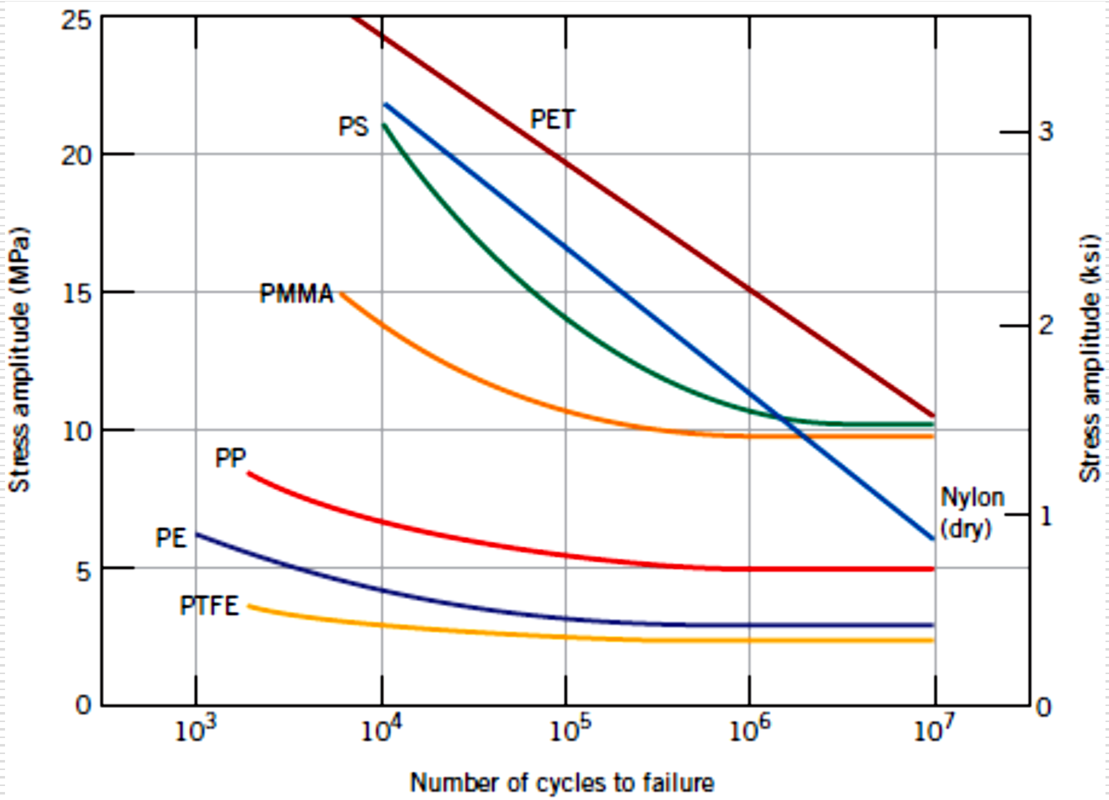
- ✓ As like metals, polymers may exhibit ductile or brittle fracture under impact loading conditions, depending on the temperature, specimen size, strain rate, and mode of loading
- ✓ Both semicrystalline and amorphous polymers are brittle at low temperatures, and both have relatively low impact strengths.
- ✓ As impact strength undergoes a gradual decrease at still higher temperatures as the polymer begins to soften.

Fatigue

✓Polymers may experience fatigue failure under conditions of cyclic loading.

✓Fatigue occurs at stress levels that are low relative to the yield strength.

✓Fatigue testing in polymers has not been nearly as extensive as with metals



Ref.- M. N. Riddell, "A Guide to Better Testing of Plastics," Plast. Eng., Vol. 30, No. 4, p. 78, 1974.

Tear Strength

Other mechanical properties that are sometimes influential in the suitability of a polymer for some particular application include tear resistance.

The ability to resist tearing is an important property of some plastics, especially those used for thin films in packaging.

Tear strength:- The mechanical parameter that is measured, is the energy required to tear apart a cut specimen that has a standard geometry. Or is a measure of how well a material can withstand the effects of tearing.

Hardness

- ✓ Another mechanical property that may be important to consider is **hardness,** which is a measure of a material's resistance to localized plastic deformation.
- ✓ Polymers are softer than metals and ceramics, and most hardness tests are conducted by penetration techniques.
- ✓ Rockwell tests are frequently used for polymers

Depth or size of an indentation

Tests:

Mohs Hardness

Rockwell Hardness

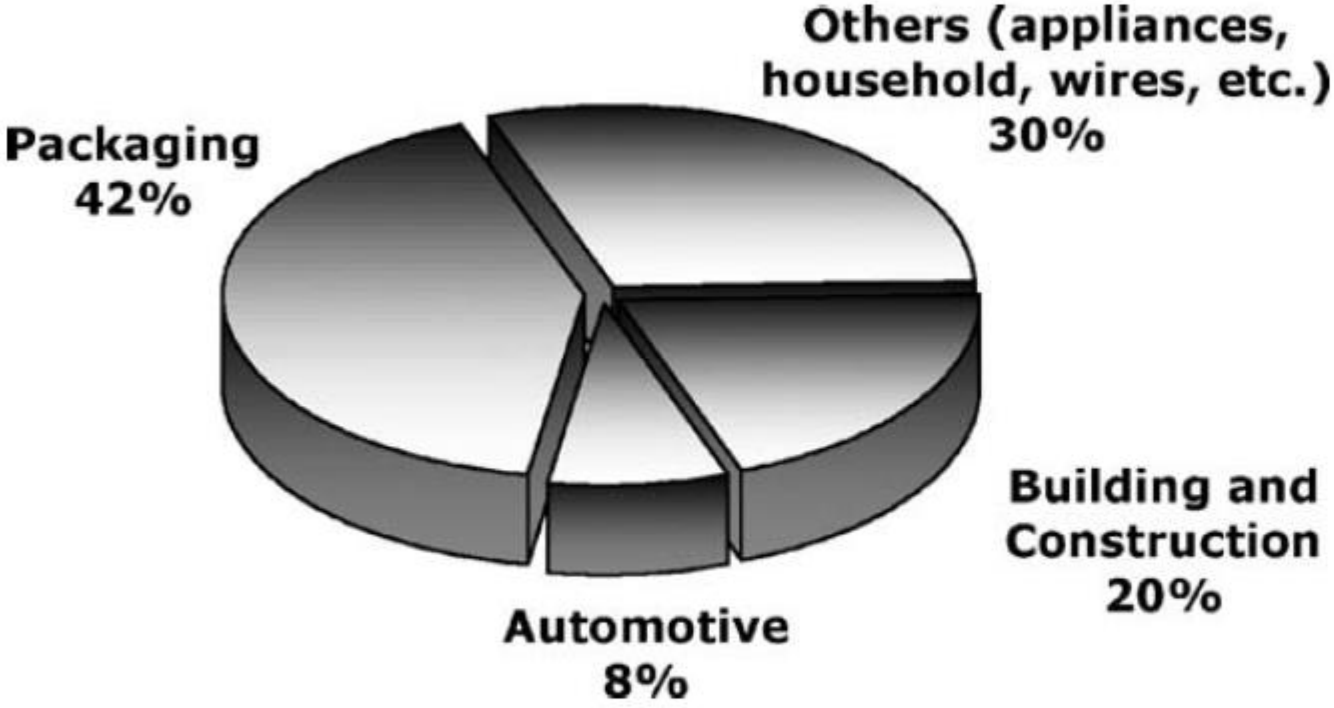
Brinell Hardness

Knoop & Vickers Microindentation Hardness

LECTURE OUTLINE

- INTRODUCTION
- THERMAL PROPERTIES
- MECHANICAL PROPERTIES
- BARRIER PROPERTIES
- OTHER PROPERTIES
- CONVENTIONAL POLYMERS IN PACKAGING
- BIO-BASED POLYMERS IN PACKAGING
- POLYMER NANOCOMPOSITES
- SUMMARY

POLYMER GLOBAL MARKET



Silvestre et al. *Prog. Polym. Sci.* **2011**, 36, 1766.

COMMON PACKAGING APPLICATIONS

- ❖ FOOD PACKAGING: FRUITS, VEGETABLES, MEAT
- ❖ WATER BOTTLES, SODA BOTTLES
- ❖ COSMETICS, CLEANING SUPPLIES

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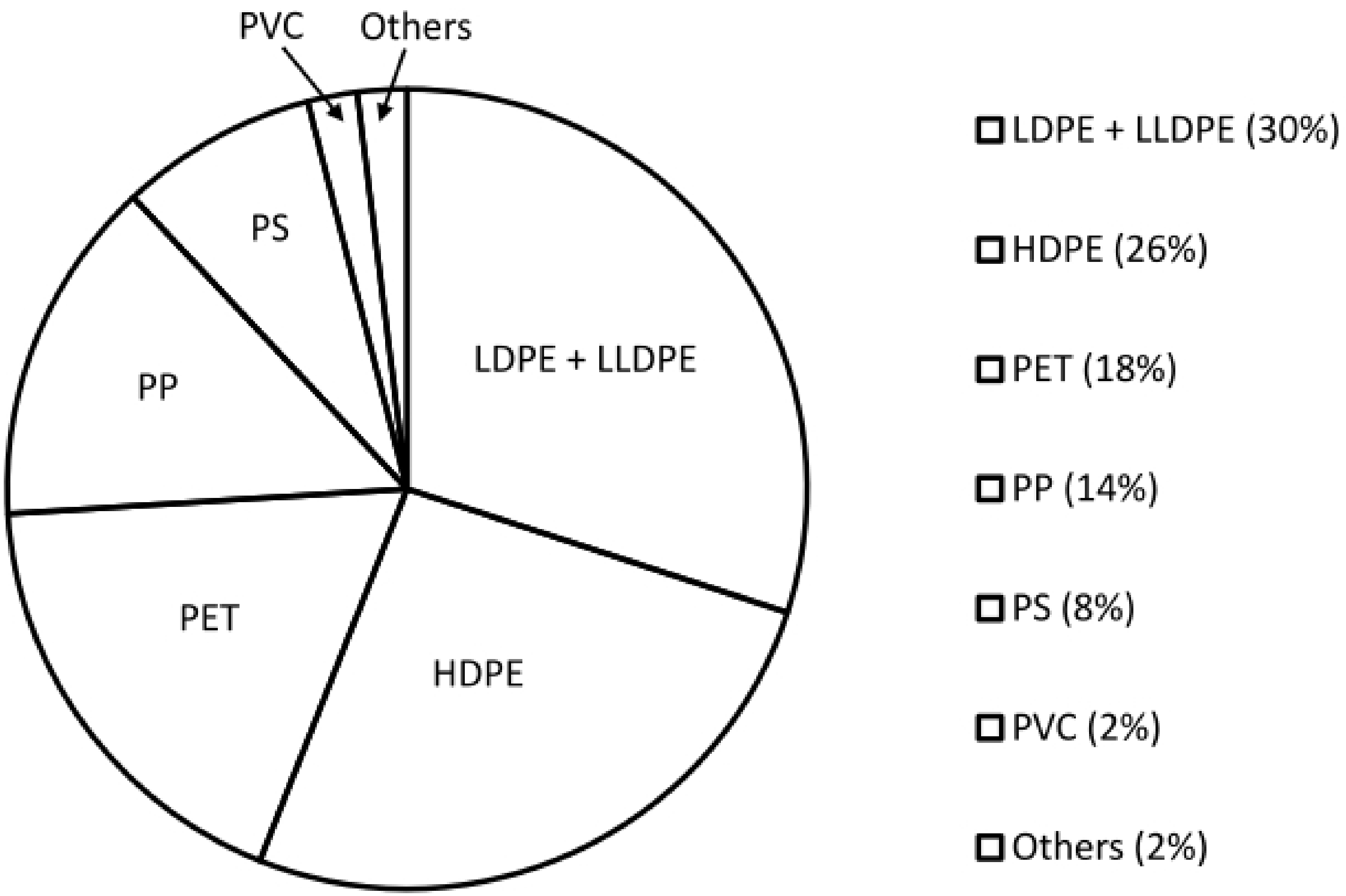
POLYMERS USED IN PACKAGING



POLYMER CRYSTALLINITY

- Most polymers are semi-crystalline.
- Crystallinity decreased with increased branching..
- Tacticity has a strong effect on crystallinity as well.
- Degree of crystallinity in turn influences several properties of polymers.

MEASURING POLYMER CRYSTALLINITY

❖ **USING X-RAY SCATTERING:**

$$x_m = \frac{A_c}{A_c + A_a}$$

❖ **USING DENSITY MEASUREMENT:**

$$x_v = \frac{\rho - \rho_a}{\rho_c - \rho_a} \qquad x_m = \frac{\rho_c}{\rho} x_v$$

EFFECT OF CRYSTALLINITY

S/N	Properties	Effect of Crystallinity
1	Density	↑
2	Tensile strength	↑
3	Clarity	↓
4	Permeability	↓
5	Opacity	↑
6	Compressive strength	↑
7	Impact strength	↓
8	Tear resistance	↓
9	Toughness	↓
10	Ductility	↓
11	Ultimate elongation	↓

THERMAL PROPERTIES

- GLASS TRANSITION TEMPERATURE
- MELTING POINT
- HEAT DISTORTION TEMPERATURE (HDT)

GLASS TRANSITION TEMPERATURE

- Temperature at which polymer transitions from glassy to rubbery state.
- Can be measured using Differential Scanning Calorimeter (DSC).
- Important in packaging applications

THERMAL PROPERTIES

HEAT DISTORTION TEMPERATURE

- Temperature at which thermoplastic begins to deflect under a specified load.
- Important in packaging applications

MELTING POINT

- Temperature at which polymer melts.
- Can be measured using Differential Scanning Calorimeter (DSC).
- Important in packaging applications

THERMAL PROPERTIES: RELATIONS

Simha and Boyer (1962): $(\alpha_l - \alpha_g)T_g = 0.113$

Bondi (1968): $\alpha_c T_m = 0.11$

Blend T_g (Fox, 1956): $$\frac{1}{T_g} = \frac{\varphi_1}{T_{g1}} + \frac{1-\varphi_1}{T_{g2}}$$

Blend T_g (Gordon-Taylor, 1952):

$$T_g = \frac{\varphi_1 T_{g1} + k_{GT}(1-\varphi_1)T_{g2}}{\varphi_1 + k_{GT}(1-\varphi_1)}$$

THERMAL PROPERTIES OF POLYMERS

Polymer	(°C)	(°C)	Mechanical Characteristics (at 25°C)
PS	240	100	Brittle
PVA	228	85	Rigid & stiff
PET	265	80	Stiff
PP (isotactic)	185	-8	May be brittle
PP (atactic)		-19	More rigid than PE
PE	105-115 (LDPE) 120-145 (HDPE)	-120	Flexible & soft

MECHANICAL PROPERTIES

- YIELD STRENGTH
- ULTIMATE TENSILE STRENGTH
- ELONGATION AT BREAK
- TOUGHNESS
- TEAR STRENGTH
- BURST STRENGTH
- IMPACT STRENGTH

YIELD STRENGTH & TENSILE STRENGTH

- ❖ **YIELD STRENGTH: Stress beyond which plastic deformation of the material begins.**
- ❖ **ELASTIC MODULUS: Slope of the stress-strain curve in the linear regime.**
- ❖ **TENSILE STRENGTH: Stress at which fracture occurs.**
- ❖ **ELONGATION AT BREAK: Value of strain at fracture.**

IMPACT STRENGTH

- **Ability of a material to withstand sudden load.**
- **High impact strength required in packaging to ensure safety of packaged product.**
- **Measured using Izod impact test and Charpy pendulum test.**

TENSILE AND IMPACT STRENGTH

Plastic	Tensile Strength (MPa)	Impact Strength (J/m)
LDPE	9-15	No break
HDPE	10- 60	30- 200
PP	1-2 (atactic)	27 (isotactic)
PS	30- 60	~ 20
PET	50	90
PC	~ 66	850

TOUGHNESS

- **Area under the stress-strain curve.**
- **Tough materials can withstand significant elongation before fracture.**
- **Rigid plastics such as polystyrene and polycarbonate are strong but not tough.**
- **Flexible plastics such as polyethylene and polypropylene are not as strong but are tougher.**

TEAR AND BURSTING STRENGTH

- **TEAR STRENGTH: Measure of how well a material can withstand tearing.**
- **Important in packaging such as stretch films**

- **BURSTING STRENGTH: Determined by pressurizing the sample until it bursts.**
- **Large bursting strength is preferable for packaging plastics.**

BARRIER PROPERTIES

- Measure of resistance to gas transmission of packaging materials.
- Extremely important in packaging applications.
- Barrier property is inversely related to gas permeability.
- Permeability, P, is defined as the ratio of penetrant flux per unit pressure gradient across a sample:

$$P = FL/\Delta P$$

- Permeability is the product of solubility and diffusivity:

$$P = DS$$

PERMEABILITY MODELS

- **Permeability from Free Volume Theory:**

$$P = Ae^{-B/(V-V_0)}$$

- **Permeability of Polymer Blends:**

$$\ln\left(\frac{P}{A}\right) = \left[\frac{\varphi_1}{\ln(P_1/A)} + \frac{\varphi_2}{\ln(P_2/A)}\right]^{-1}$$

- **Permeability of Multilayer Films:**

$$P_{overall} = L\left(\sum_{i=1}^{n} \frac{l_i}{P_i}\right)^{-1}$$

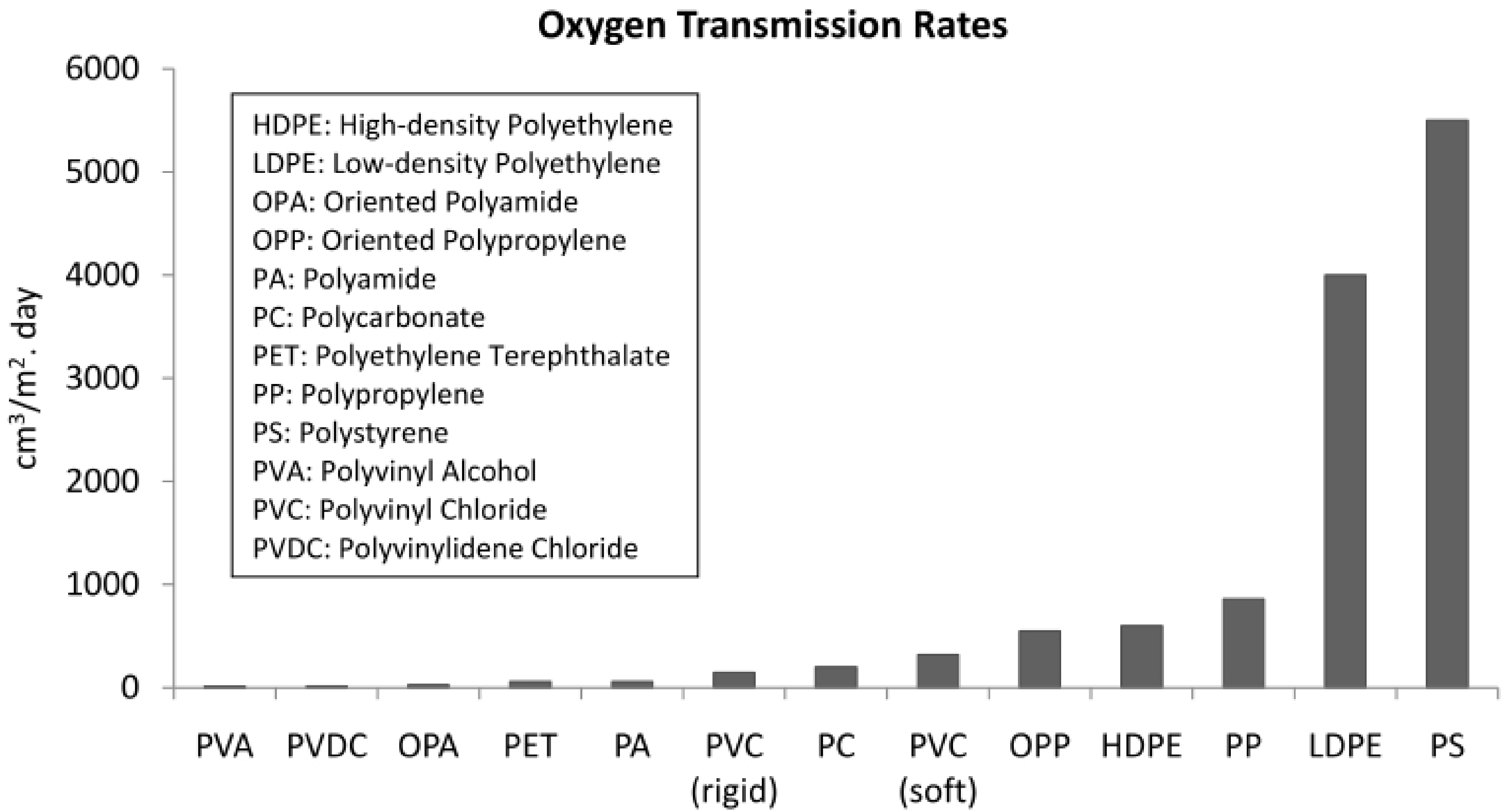
Paul, D. R. *J. Membr. Sci.*, **1984**, 18, 75.

Jang et al., *Appl. Phys. Lett.*, **2008**, 93, 133307.

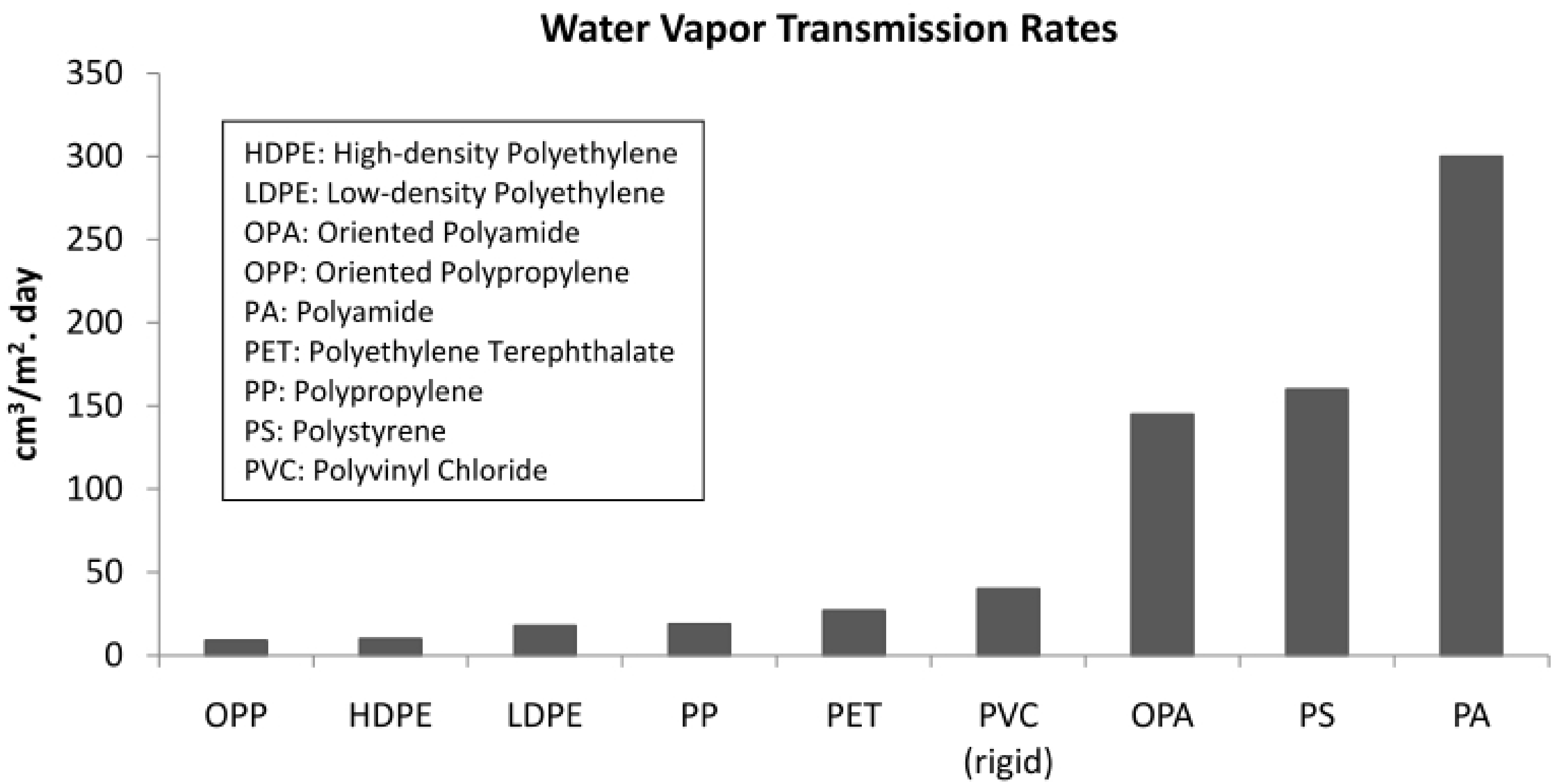
GAS PERMEABILITY

- Following are of special interest:
  - OXYGEN TRANSMISSION RATE
  - WATER VAPOR TRANSMISSION RATE
  - CO_2 TRANSMISSION RATE
- Good oxygen and water vapor barrier properties are desirable to ensure no deterioration in food quality.
- Some respiring products may require packaging that allow the transmission of gases.
- Soda bottles must be impermeable to CO_2.

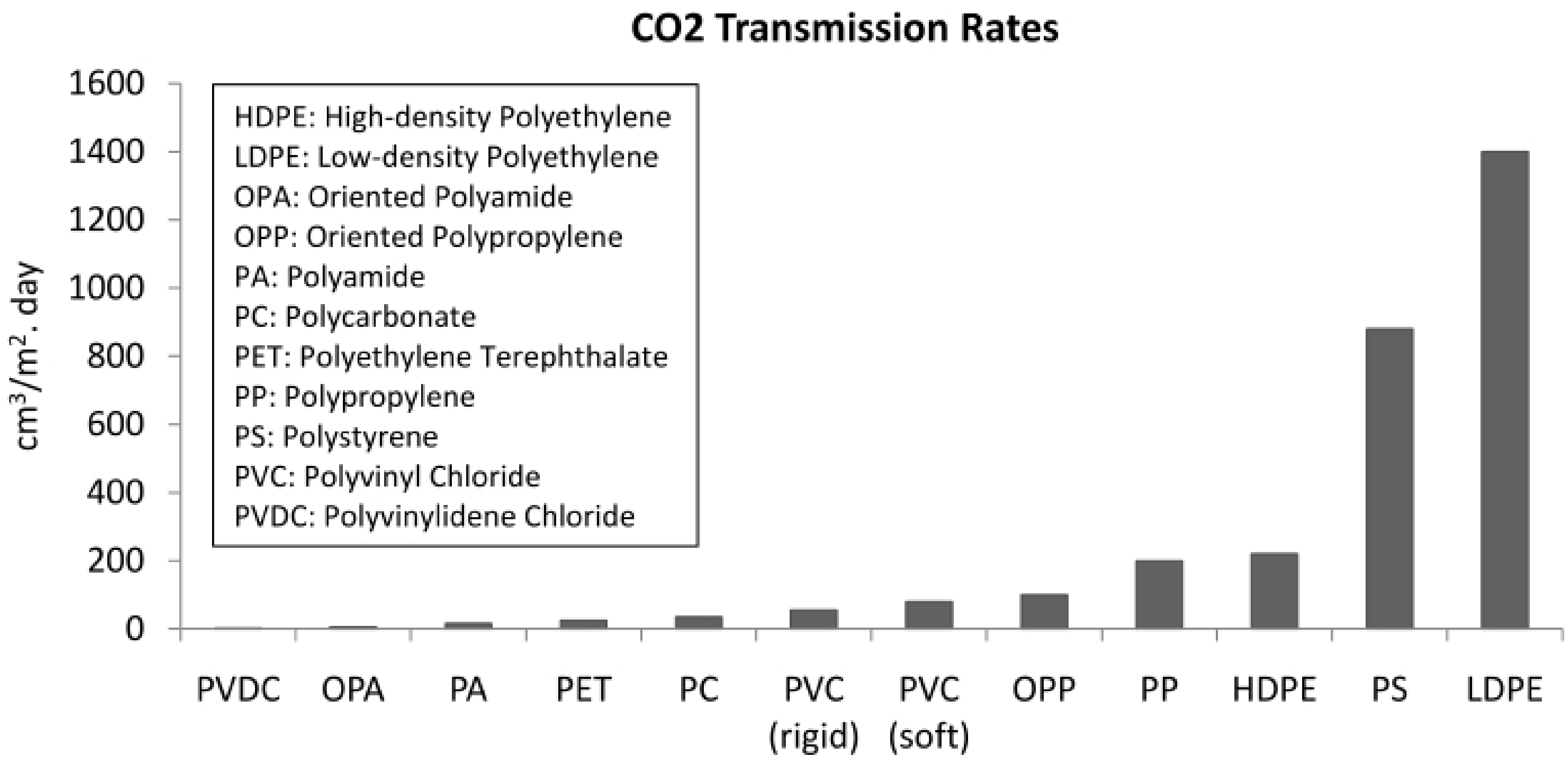
OXYGEN TRANSMISSION RATES



WATER VAPOR TRANSMISSION RATES



CO_2 TRANSMISSION RATES



OTHER PROPERTIES: OPTICAL

- **TRANSPARENCY:**
  - **Decreases with increasing crystallinity.**
  - **Transparent plastics may be used in place of glass.**

- **GLOSS:**
  - **Specular reflection leads to glossy appearance.**
  - **Glossy packaging may enhances aesthetic appeal.**

CONVENTIONAL POLYMERS: POLYETHYLENE (PE)

- Most common packaging plastic.
- Tough and flexible, good water vapor barrier.
- Free from odor and is non-toxic.
- Higher crystallinity in PE leads to improved hardness, tensile strength, opacity, barrier properties.
- Used in packaging of bakery, meat, poultry, dairy products etc.

CONVENTIONAL POLYMERS: POLYETHYLENE (PE)

Type of Polyethylene	Density (g/cm^3)	(˚C)
High density polyethylene (HDPE)	0.94-0.96	120-145
Medium density polyethylene (MDPE)	0.93-0.94	
Low density polyethylene (LDPE)	0.91-0.93	105-115
Linear low density polyethylene (LLDPE)	0.91-0.93	120-125
Very low density polyethylene (VLDPE)	0.89-0.91	
Ultra low density polyethylene (ULDPE)	<0.89	50-75

CONVENTIONAL POLYMERS: POLYPROPYLENE (PP)

- ❖ **Used extensively in packaging applications.**
- ❖ **Higher thermal resistance than PE.**
- ❖ **PP is non-toxic, has good mechanical properties and excellent clarity.**
- ❖ **Has poor oxidative stability.**

CONVENTIONAL POLYMERS: POLYSTYRENE (PS)

- **Good chemical resistance and electrical insulation.**
- **Free from odor and is non-toxic.**
- **PS foam is good thermal insulator.**
- **Pure PS is brittle.**

CONVENTIONAL POLYMERS: POLYETHYLENE TEREPHTHALATE

- **Excellent gas barrier properties.**
- **Crystalline PET has good strength, rigidity and thermal resistance.**
- **High glass transition temperature and melting temperature.**
- **PET bottles extensively used in packaging carbonated soda.**

BIO-BASED POLYMERS: STARCH

- Can be derived from renewable resources.
- Relative amount of amylose and amylopectin determine properties.
- Low oxygen permeability and low cost.
- Hydrophilic and poor mechanical properties.

BIO-BASED POLYMERS: CELLULOSE

- **Cellulose is converted to cellophane for packaging use.**

- **Cellophane has good mechanical properties, is sensitive to moisture.**

- **Cellulose is also converted to cellulose acetate.**

BIO-BASED POLYMERS: CHITOSAN

- **Is biodegradable, biocompatible and non-toxic.**

- **Transparent, tough, flexible films with good oxygen barrier properties.**

- **Shows antimicrobial activity.**

- **Poor water vapor barrier property.**

BIO-BASED POLYMERS: POLY(LACTIC ACID)

- One of the most promising bio-based polymers.
- Has good mechanical properties and is biocompatible.
- High melting point compared to other biodegradable plastics .
- Has the potential to replace conventional plastics.

POLY(LACTIC ACID) PROPERTIES

Property	Experimental value
Glass transition temperature (T_g °C)	62.1 ±0.7
Melting temperature (T_m °C)	150.2 ±0.5
Tensile Strength (MPa)	48 to 53
Oxygen transmission rate (OTR) at 23°C and 0% relative humidity (RH) (cc / (m^2·day))†	56.33 ±0.12
Oxygen permeability coefficient (OPC) at 23°C and 0% RH (kg·m / (m^2·s·Pa))†	$4.33 \times 10^{-18} \pm 1.00 \times 10^{-19}$
Water vapor transmission rate (WVTR) at 37.8 °C and 100 % RH (g / (m^2·day)) †	15.30 ± 0.04
Water vapor permeability coefficient (WVPC) at 37.8 °C and 100 % RH (kg·m / (m^2·s·Pa)) †	$1.34 \times 10^{-14} \pm 3.61 \times 10^{-17}$

Auras et al. *J. Testing Eval*, **2006**, 34, 1.

Jamshidian et al. *Rev. Food Sci. Food Safety*, **2010**, 9, 552.

BIO-BASED POLYMERS: POLYHYDROXYALKANOATES

- Several polyhydroxyalkanoates with a wide range of properties can be synthesized.

- Polyhydroxybutyrate is the most common polyhydroxyalkanoate.

- Exhibits low water vapor permeability.

- Good thermal and mechanical properties.

POLYMER NANOCOMPOSITES IN PACKAGING

- Nanocomposites can improve the thermo-mechanical and gas barrier properties of synthetic and bio-based polymers.

- Commonly used filler materials include clays (e.g. montmorillonite), nanoparticles, nanotubes, graphene etc.

- Cellulose nanocrystals (CNC) can also be incorporated as filler material.

SUMMARY

- **Thermo-mechanical and gas barrier properties critical in packaging applications of plastics.**

- **Bio-based plastics are promising candidates for environment-friendly packaging materials.**

- **Polymer nanocomposites often show property enhancement over neat polymer.**

THANK YOU