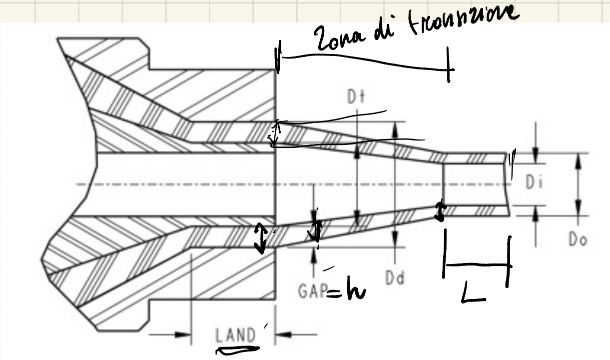
Lezione 15 08.11.2022

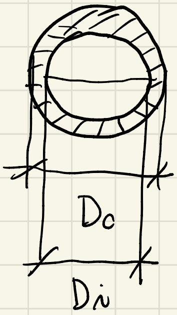
- Equazione WLF e la teoria del volume libero
- Die-swell e Numero di Deborah
- Introduzione alle proprietà meccaniche

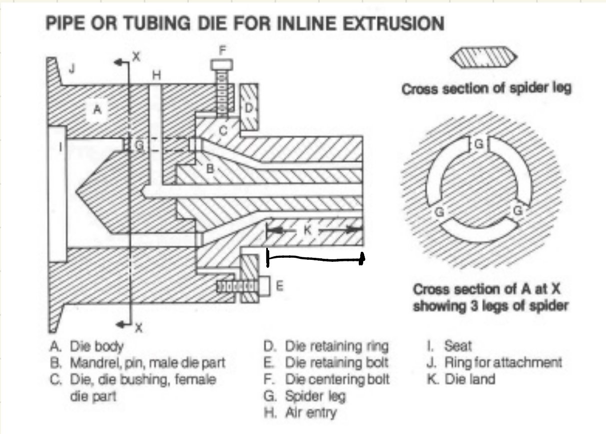
h = Die Gap

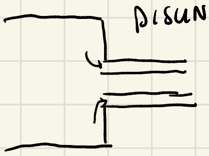


$$K = \frac{2\pi (R_i + R_o) h^3}{12 L}$$

$$\dot{\gamma} = \frac{6Q}{\pi (R_i + R_o) h^2}$$







DISUNIFORMITÀ SPESSORE FINITURE

Equazione WLF : METODO SPERIMENTALE UTILE PER PARAMETRIZZARE UNA GRANDEZZA FISICA

↓

William-Landel-Ferry

η , E , D

$$\log a_T = \log \frac{\eta(T)}{\eta(T_R)} = \frac{-C_1 (T-T_R)}{C_2 + (T-T_R)}$$

Se $T_R = T_G$ e $T_G < T < T_G + (150 \div 200°C)$

$C_1 = 17.4$

$C_2 = 51.6$ K o °C

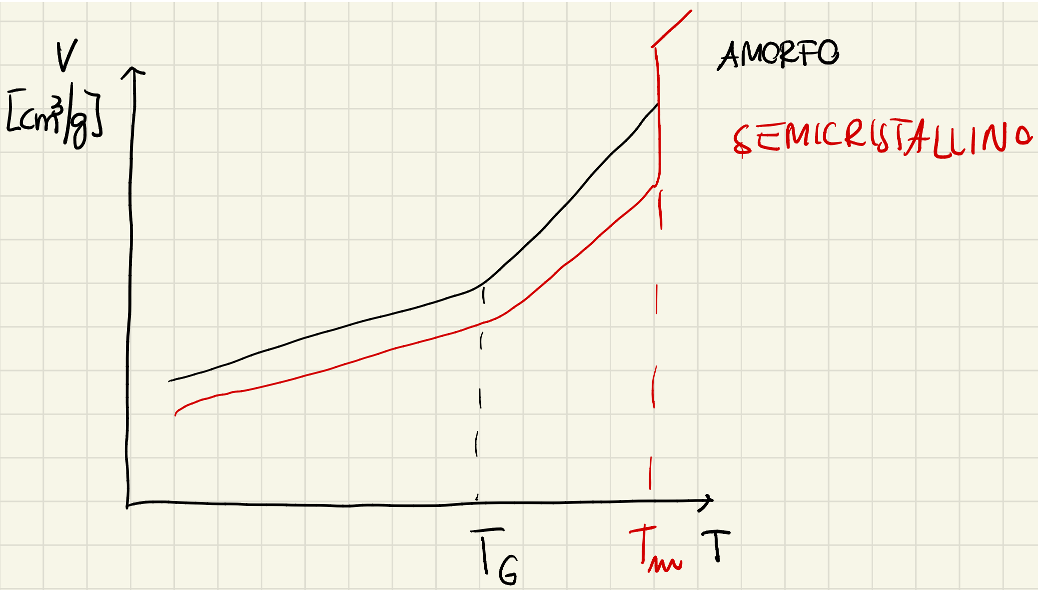
} Ricavati sperimentalmente

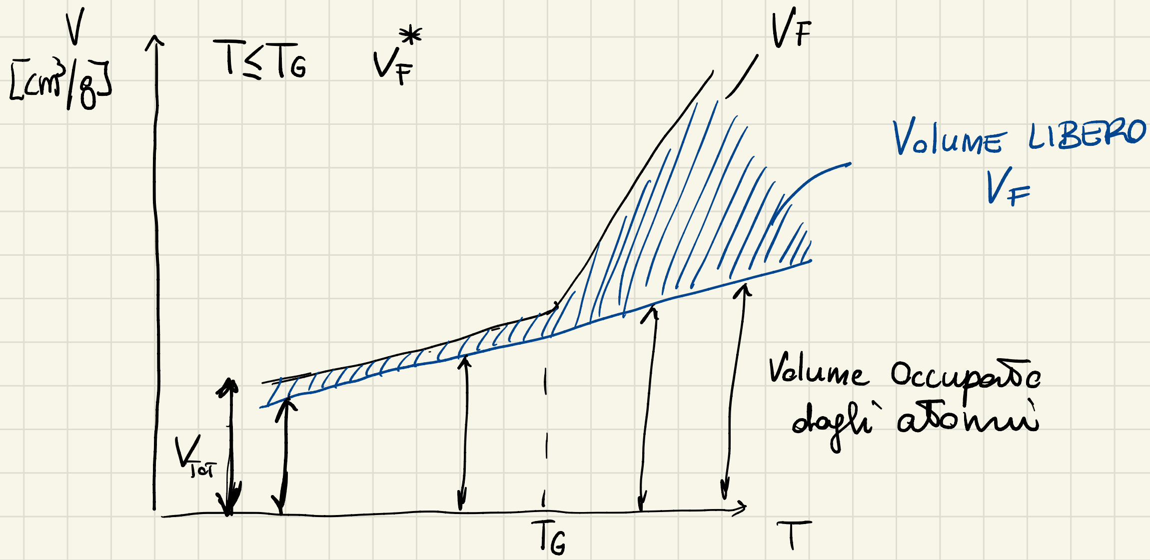
POLIMERI TERMOPLASTICI AMORFI e ELASTOMERI

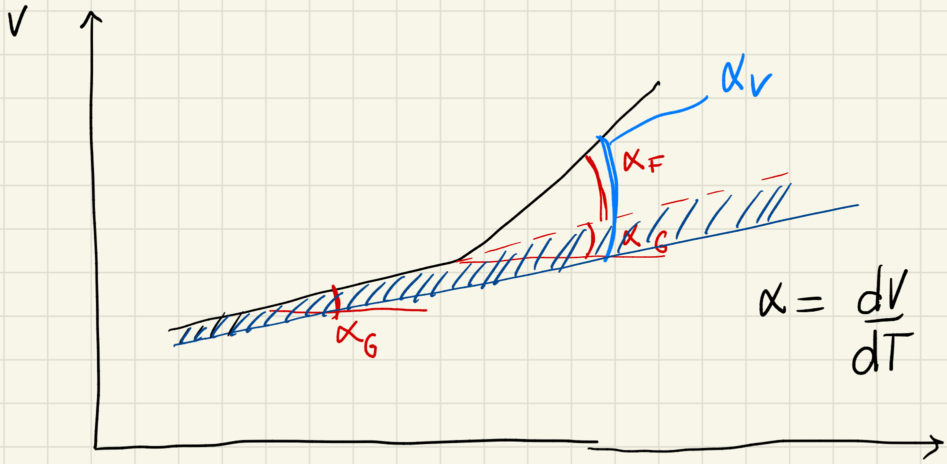
ELASTOMERI:

- AMORFI $T > T_G$
- $X_c \to 0$
- Possono parzialmente reticolare

VOLUME LIBERO → V [cm³/g] vs T


V
[cm³/g]
AMORFO
SEMICRISTALLINO
T_G
T_m
T


V
[cm³/g]
T≤T_G
V_F*
V_F
Volume LIBERO
V_F
Volume Occupato dagli atomi
V_TOT
T_G
T



$$\alpha_F = \alpha_V - \alpha_G$$

Definisco F = FRAZIONE di VOLUME LIBERO

$$F = \frac{V_F}{V}$$

$$F_G = \frac{V_F^*}{V}$$

$$F(T) = F_G + (T - T_G)\,\alpha_F$$

F_G → FRAZIONE di VOLUME LIBERO per $T \leq T_G$

$F_G = 0{,}025$

$\alpha_F = 4.8 \times 10^{-4}\,K^{-1}$

$$\eta(T) = A\, e^{\frac{B}{T - T_G}}$$

RICAVATA SPERIMENTALMENTE DA DOOLITTLE

$$\eta(T) = A e^{B \frac{V - V_F}{V_F}} \qquad F = \frac{V_F}{V}$$

$$= A e^{B\left(\frac{1}{F} - 1\right)}$$

$$\ln \eta(T) = \ln A + B\left(\frac{1}{F} - 1\right)$$

$$\log a_T = \log \frac{\eta(T)}{\eta(T_R)}$$

$$\log \frac{\eta(T)}{\eta(T_G)} = \log a_T = \frac{-(B/2.303 F_g)(T - T_G)}{F_G/\alpha_F + (T - T_G)}$$

C_1

C_2

$C_2 = 51.6$ K

$$C_2 = \frac{0.025}{4.8 \times 10^{-4} \, (K^{-1})}$$

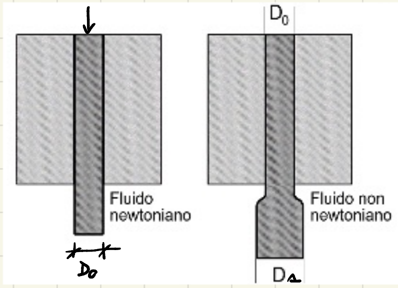
$$= \frac{0.025 \times 10^4}{4.8} = \frac{250}{4.8} \simeq 52 \text{ K}$$

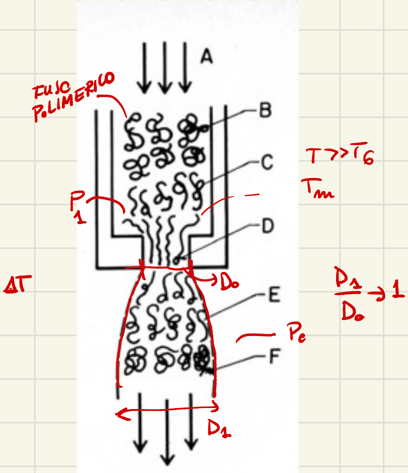
De → Numero di Deborah

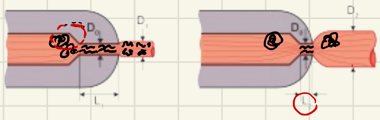
$$N_D = \frac{\text{response time of the material}}{\text{experimental or observation time}}$$

response time of the material → τ_{RIL} / λ

Die-Swell   Rigonfiamento

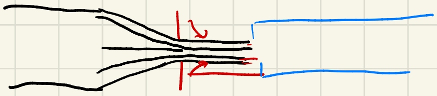






TEMPO di RILASSAMENTO del POLIMERO τ_{RIL} [s] λ [s]

↓ Tempo necessario alle macromolecole per ripristinare la conformazione a gomitolo statistico



FLUIDO VISCO-ELASTICO   FLUIDO NEWTONIANO

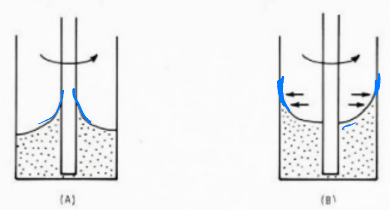
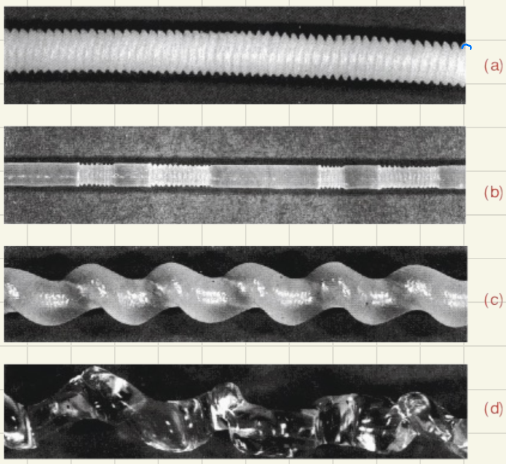


Figure 32. A, Sketch indicating the Weissenburg or rod climbing effect of a viscoelastic fluid caused by rotation of the rod in the fluid. B, Sketch showing how a Newtonian fluid "climbs" the outside of the stirring vessel due to centrifugal force.

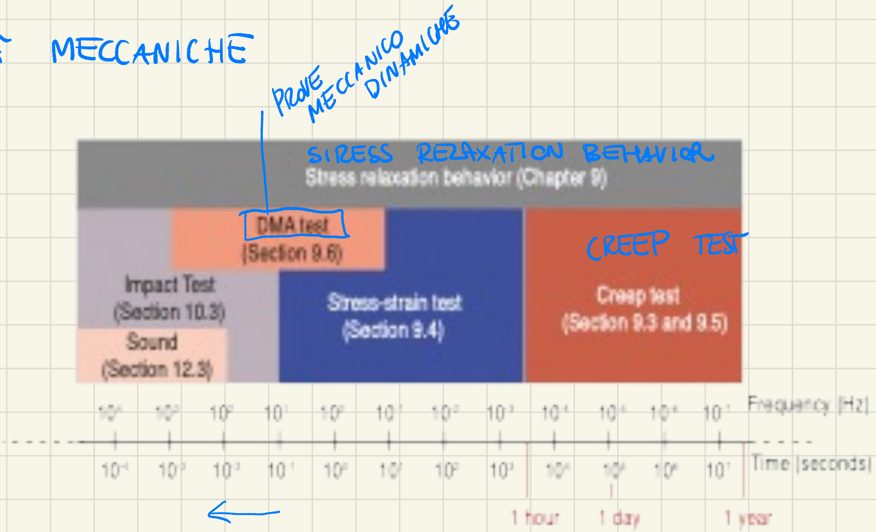
EFFETTO WEISSENBERG

SHARK SKIN o SHARK TALE



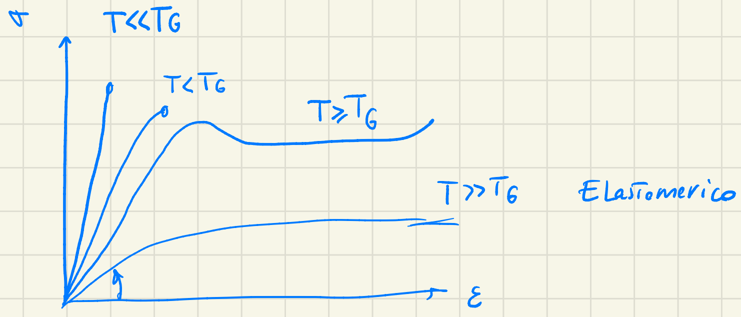
$\dot{\gamma}$, T, ΔP, η | L, h / D_i, D_o

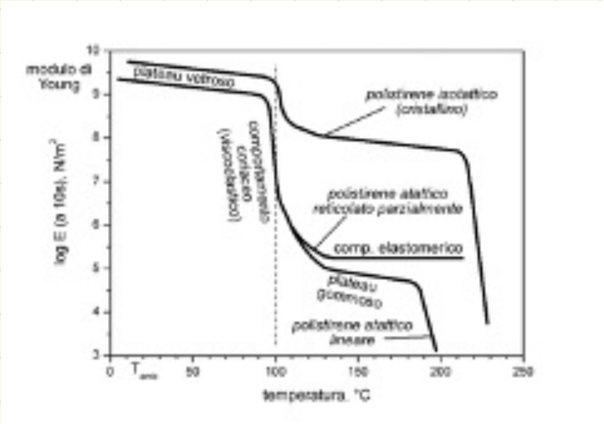
PROPRIETÀ MECCANICHE

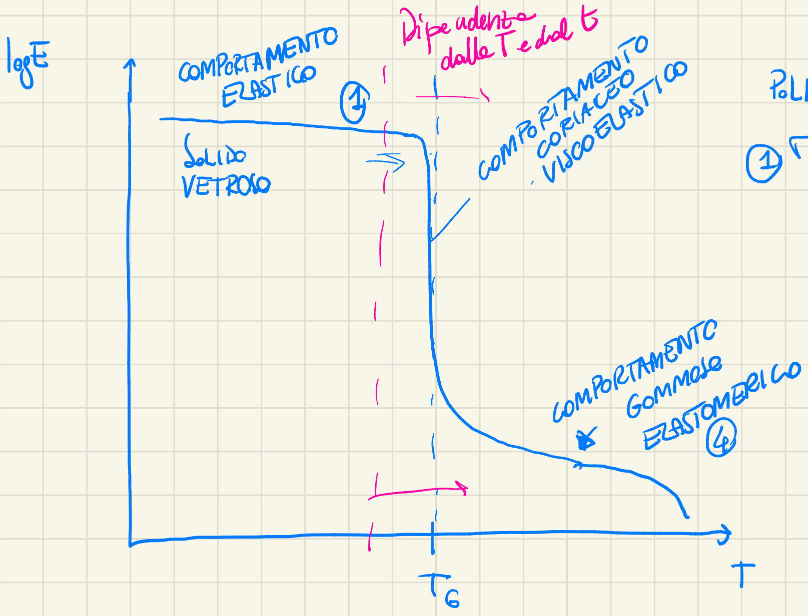


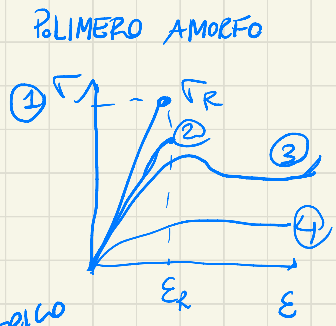
t → VELOCITÀ della PROVA

T → TEMPERATURA




modulo di Young
log E (a 10s), N/m²
plateau vetroso
polistirene isotattico (cristallino)
comportamento coriaceo (viscoelastico)
polistirene atattico reticolato parzialmente
comp. elastomerico
plateau gommoso
polistirene atattico lineare
T amb
temperatura, °C


logE
COMPORTAMENTO ELASTICO
①
Dipendente dalle T e dal t
COMPORTAMENTO CORIACEO VISCOELASTICO
SOLIDO VETROSO
COMPORTAMENTO GOMMOSO ELASTOMERICO ④
T
T_G


POLIMERO AMORFO
① σ
σ_R
②
③
④
ε_R
ε