

Anyagtudomány

BMEGEMTNG11 BMEGEMTNX11, 4 krp (2+0+1/v)

VIII-IX. előadás: Polimerek üveges átmeneti hőmérséklete,
Polimerek alakemlékező tulajdonsága

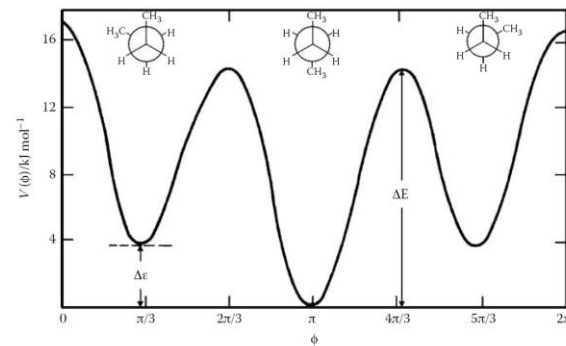
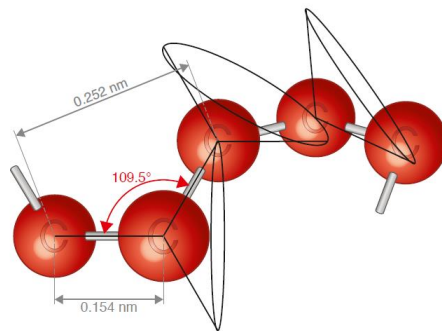
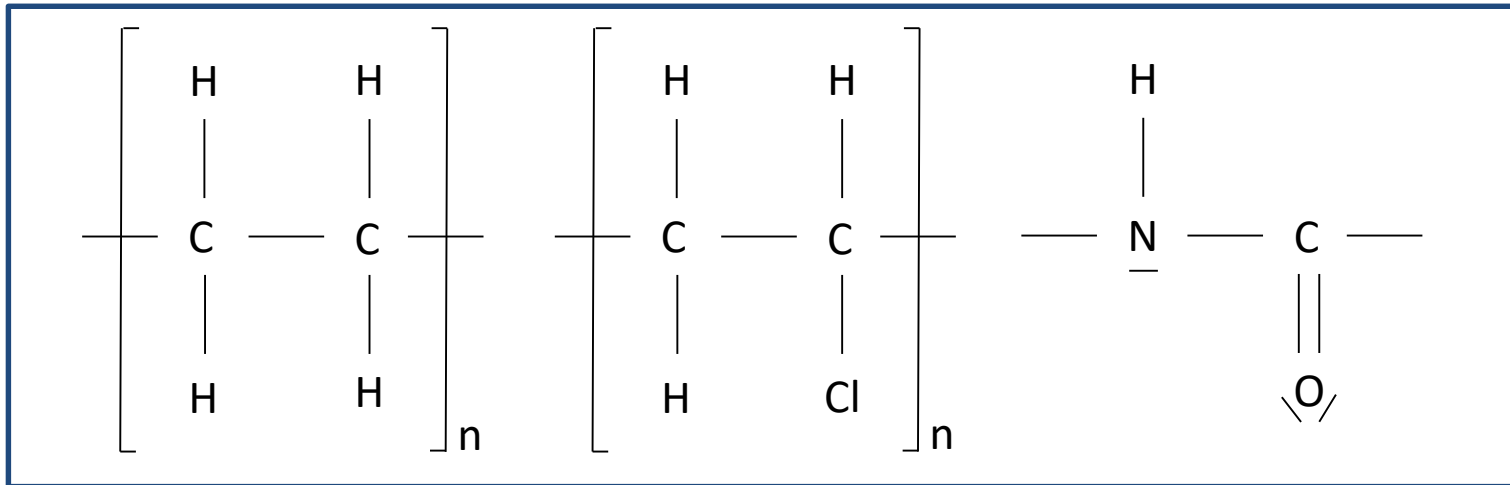
Előadó:
Dr. Mészáros László
Egyetemi docens

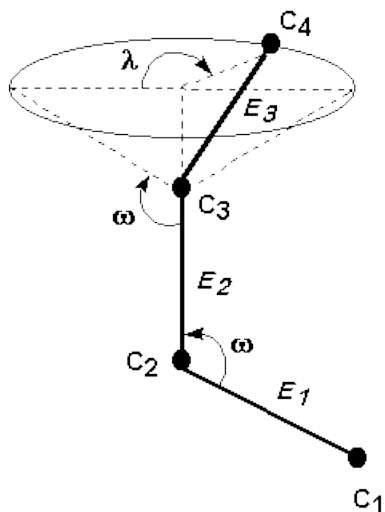
Elérhetőség:
T. ép.: 307.
meszaros@pt.bme.hu

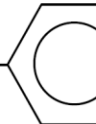
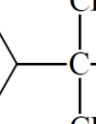

POLIMERTECHNIKA
TANSZÉK



2024. április 17, 24.





<i>Polimer</i>	<i>Ismétlődő egység</i>	T_g ($^{\circ}\text{C}$)
<i>Poli(dimetil-sziloxán)</i>	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---Si---O---} \\ \\ \text{CH}_3 \end{array}$	-123
<i>Polietilén</i>	$\text{---CH}_2\text{---CH}_2\text{---}$	-120
<i>Polioximetilén</i>	$\text{---CH}_2\text{---O---}$	-50
<i>Poliamid 6</i>	$\text{---NH---(CH}_2)_5\text{---CO---}$	50
<i>Poli(etilén-tereftalát)</i>	$\text{---OCH}_2\text{CH}_2\text{OOC---}$  ---CO---	69
<i>Polikarbonát</i>	$\text{---O---C(=O)---O---}$  $\text{---C(CH}_3)_2\text{---}$ 	150



Főlánc felépítése



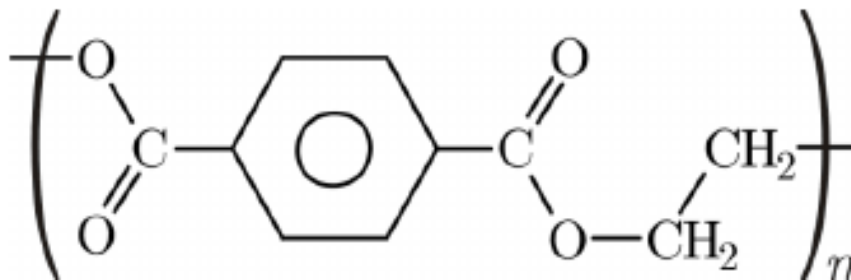
PET/PETE GRANULES



DRINKING BOTTLES



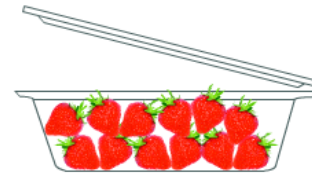
ASSORTED CONTAINERS



MICROWAVABLE TRAYS



FRUIT CONTAINERS



SYNTHETIC CLOTHES

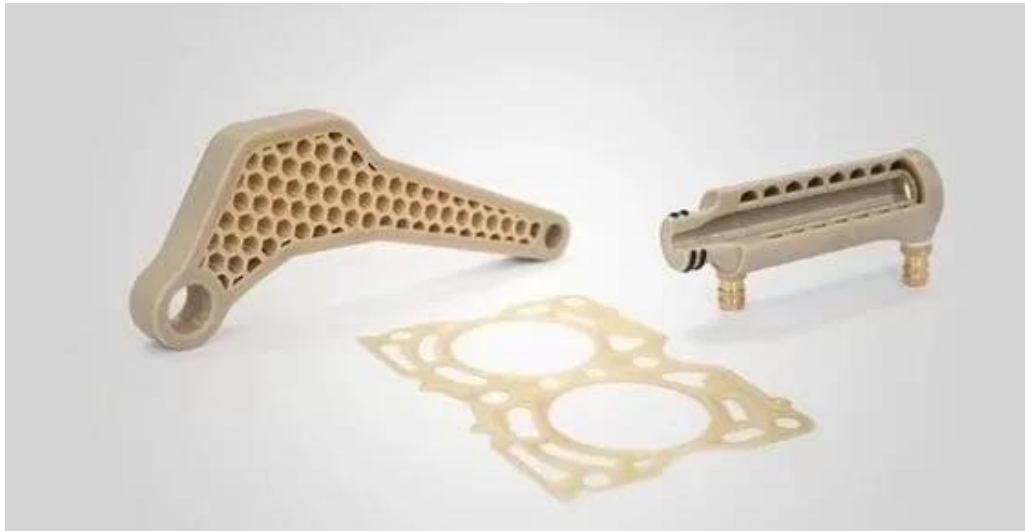
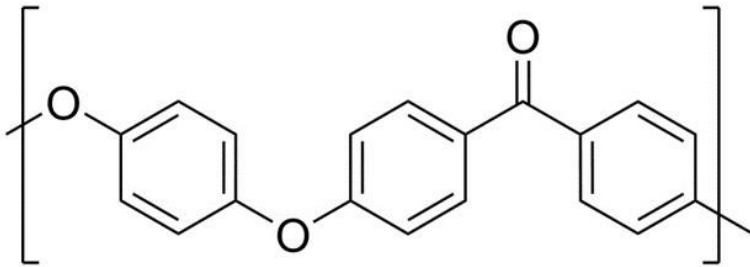


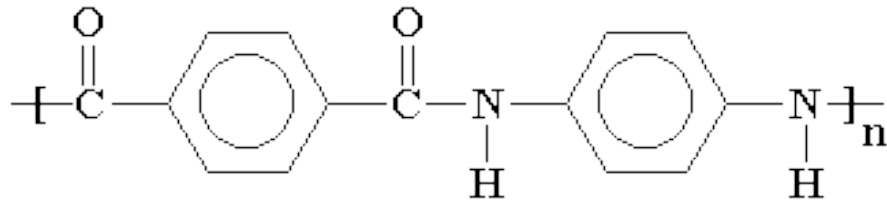
SYNTHETIC CARPET



Type 1 - PETE Polyethylene Terephthalate (PET)

Poli(éter-éter-keton) (PEEK)





<i>Polimer</i>	<i>Ismétlődő egység</i>	T_g (°C)
<i>Polietilén</i>	$\text{—CH}_2\text{—CH}_2\text{—}$	-120
<i>Polipropilén</i>	$\begin{array}{c} \text{—CH}_2\text{—CH—} \\ \\ \text{CH}_3 \end{array}$	-10
<i>Polisztirol</i>	$\begin{array}{c} \text{—CH}_2\text{—CH—} \\ \\ \text{C}_6\text{H}_5 \end{array}$	100
<i>Poli(vinil-karbazol)</i>	$\begin{array}{c} \text{—CH}_2\text{—CH—} \\ \\ \text{N} \\ \\ \text{C}_6\text{H}_4 \end{array}$	208

<i>Polimer</i>	<i>Ismétlődő egység</i>	T_g (°C)
<i>Poliizobutilén</i>	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C---} \\ \\ \text{CH}_3 \end{array}$	-65
<i>Polipropilén</i>	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{CH}_3 \end{array}$	-10
<i>Poli(vinilidén-klorid)</i>	$\begin{array}{c} \text{Cl} \\ \\ \text{---CH}_2\text{---C---} \\ \\ \text{Cl} \end{array}$	-17
<i>Poli(vinil-klorid)</i>	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{Cl} \end{array}$	80
<i>Poli(akril-nitril)</i>	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{CN} \end{array}$	130

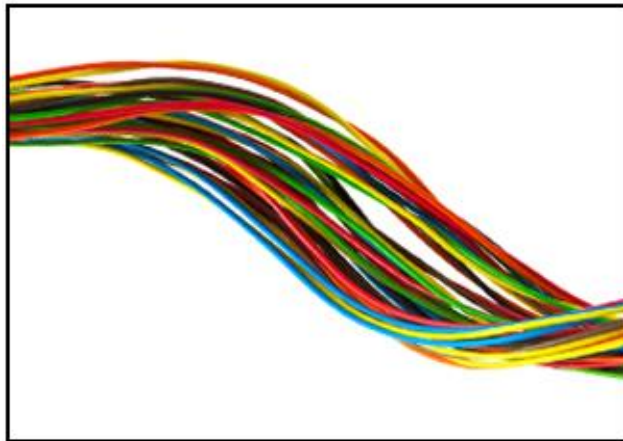


T_g különböző poliamidok esetén

Poliamid 6 $[-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-]_n$

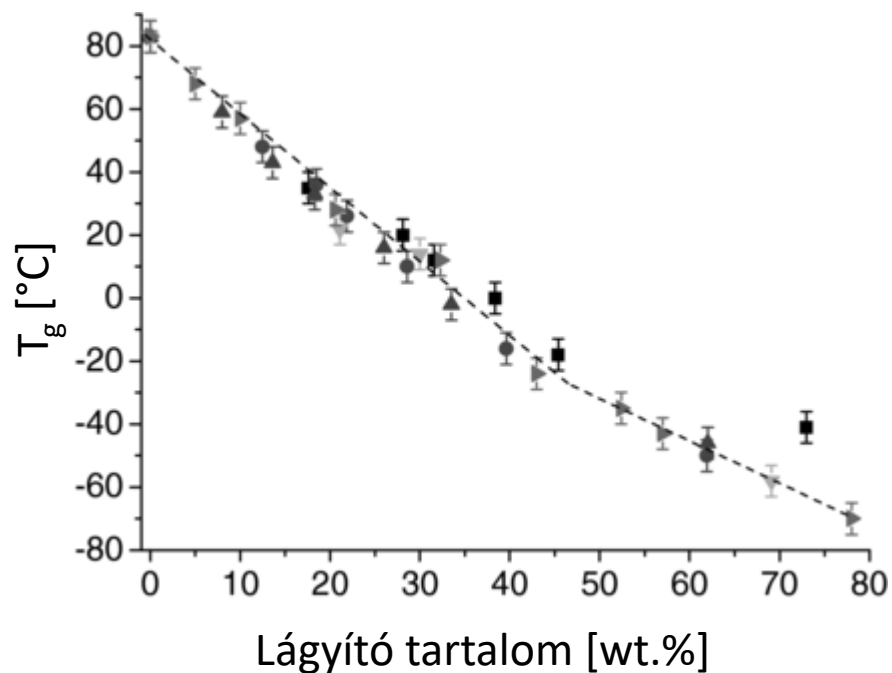
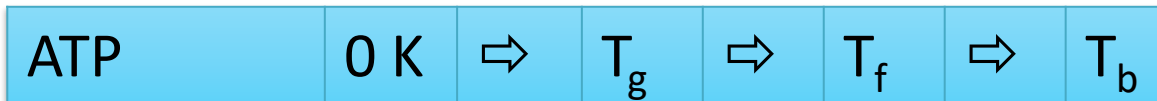
Poliamid 12 $[-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-]_n$

Poliamid típusa	T _g [°C]
PA 3	107
PA 6	51
PA 8	49
PA 10	42
PA 11	41
PA 12	40

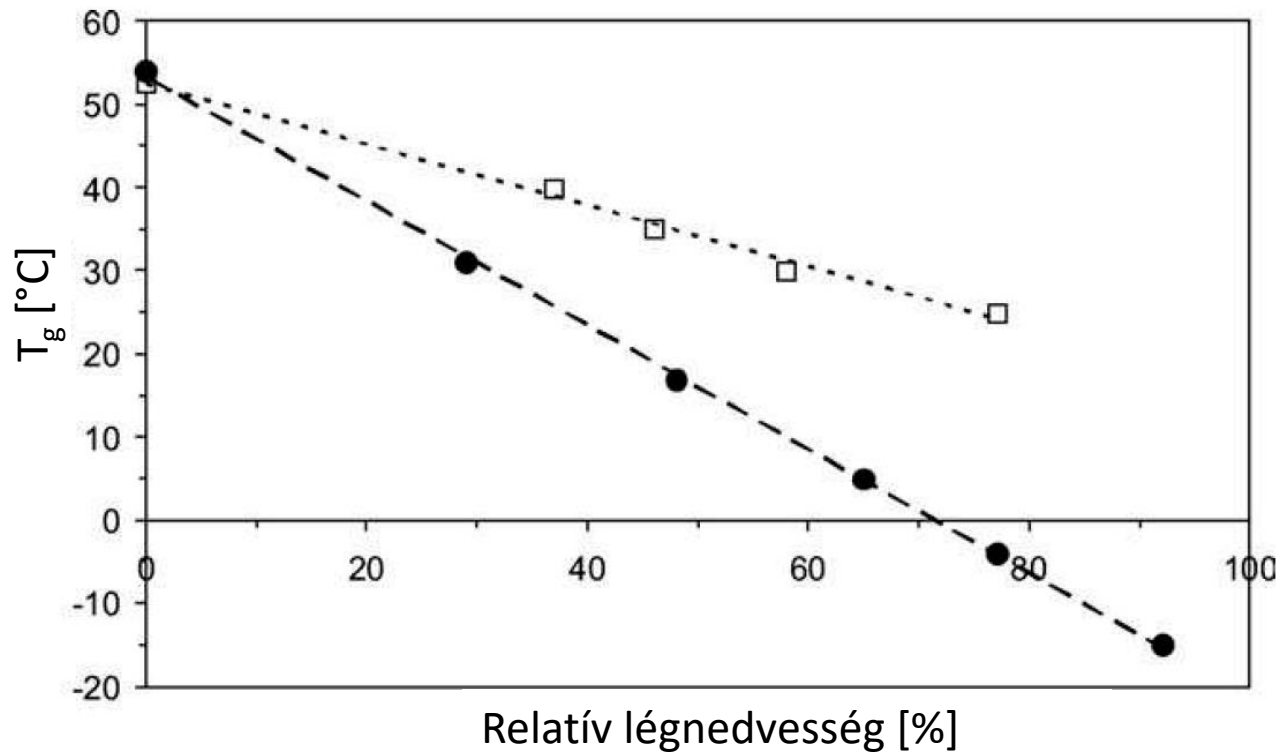




A lágyítótartalom hatása

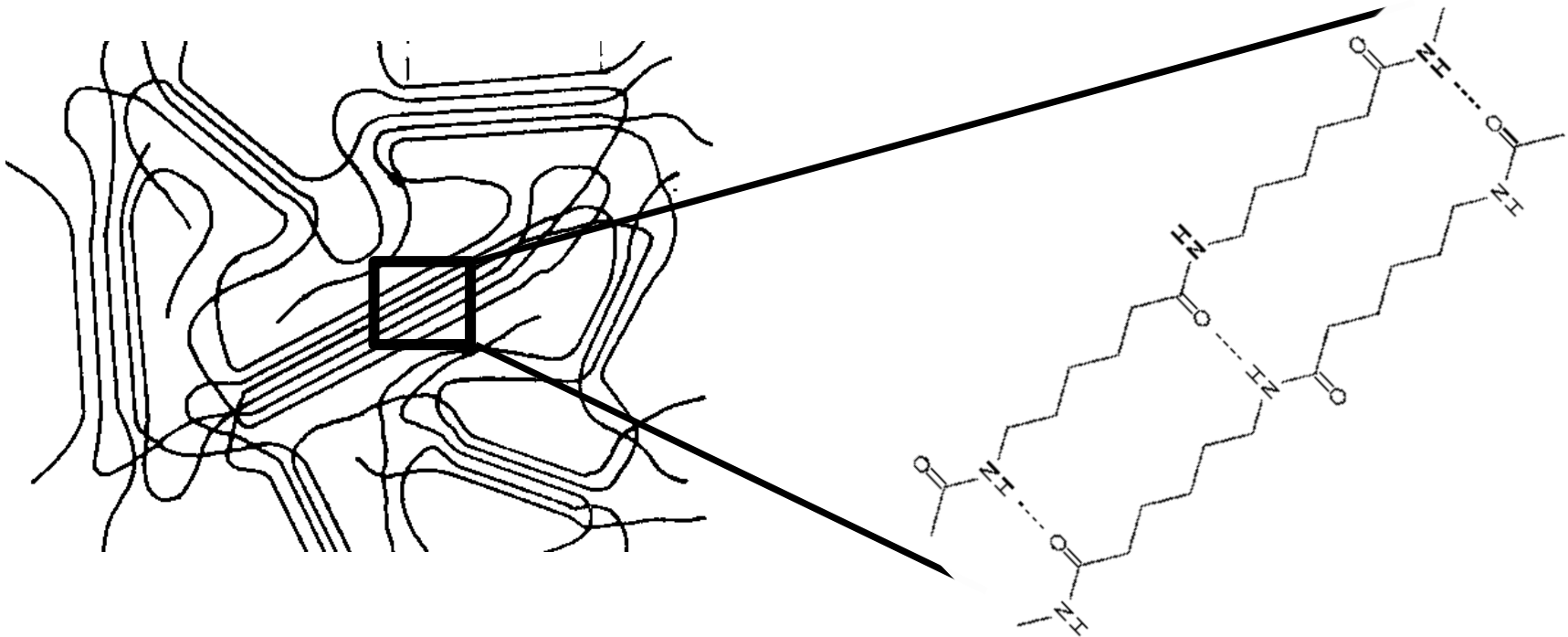


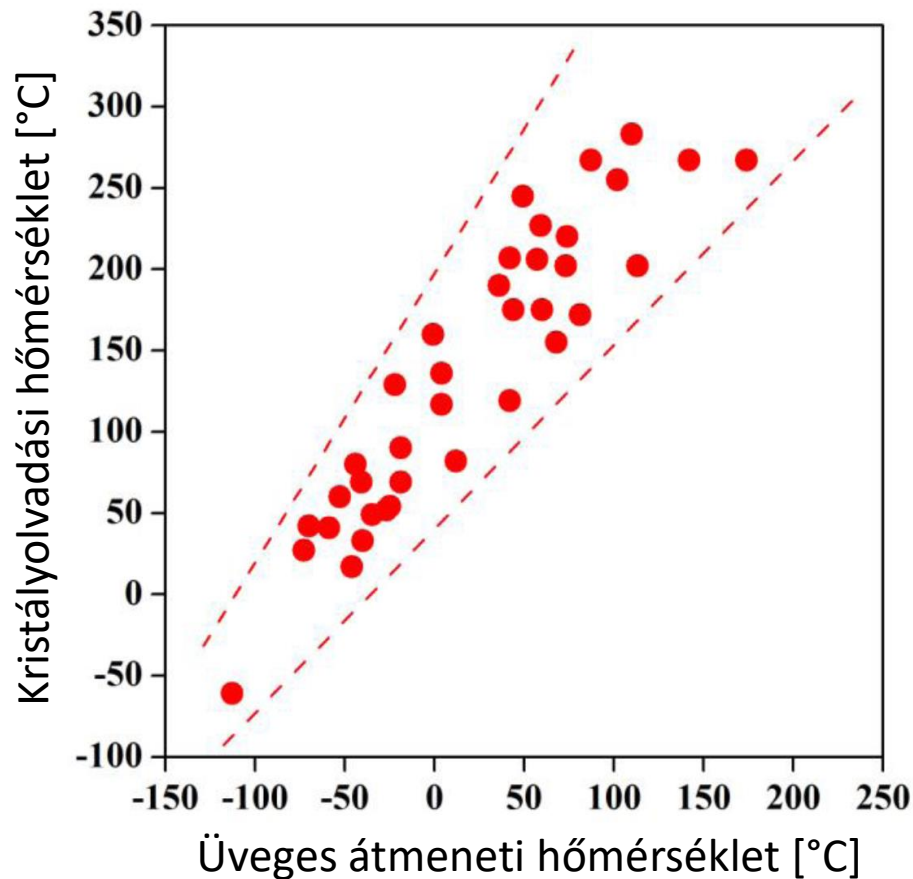
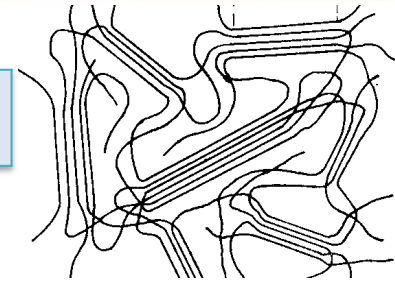
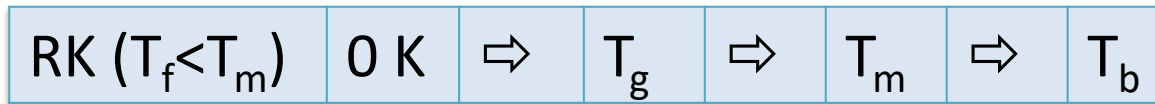
- PA 6 $[-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-]_n$
- PA 6.12 $[-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-]_n$



Hatzigrigoriou N. B., Vouyiouka S. N., Joly C., Dole P., C. D. Papaspyrides C. D.:
 Temperature-humidity superposition in diffusion phenomena through polyamidic materials.
 Journal of Applied Polymer Science, 125, 2814-2823 (2012).

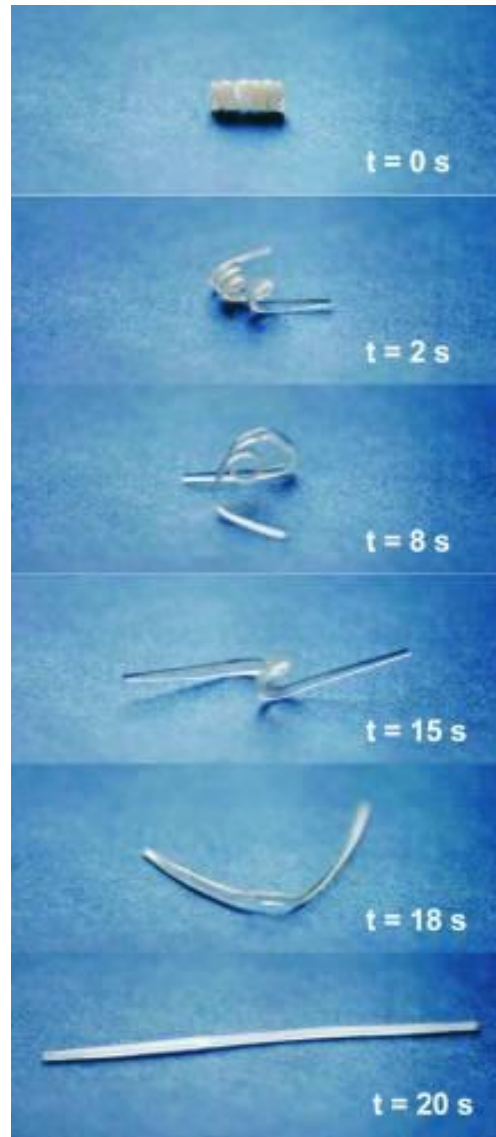
RK ($T_f < T_m$) 0 K \Rightarrow T_g \Rightarrow T_m \Rightarrow T_b

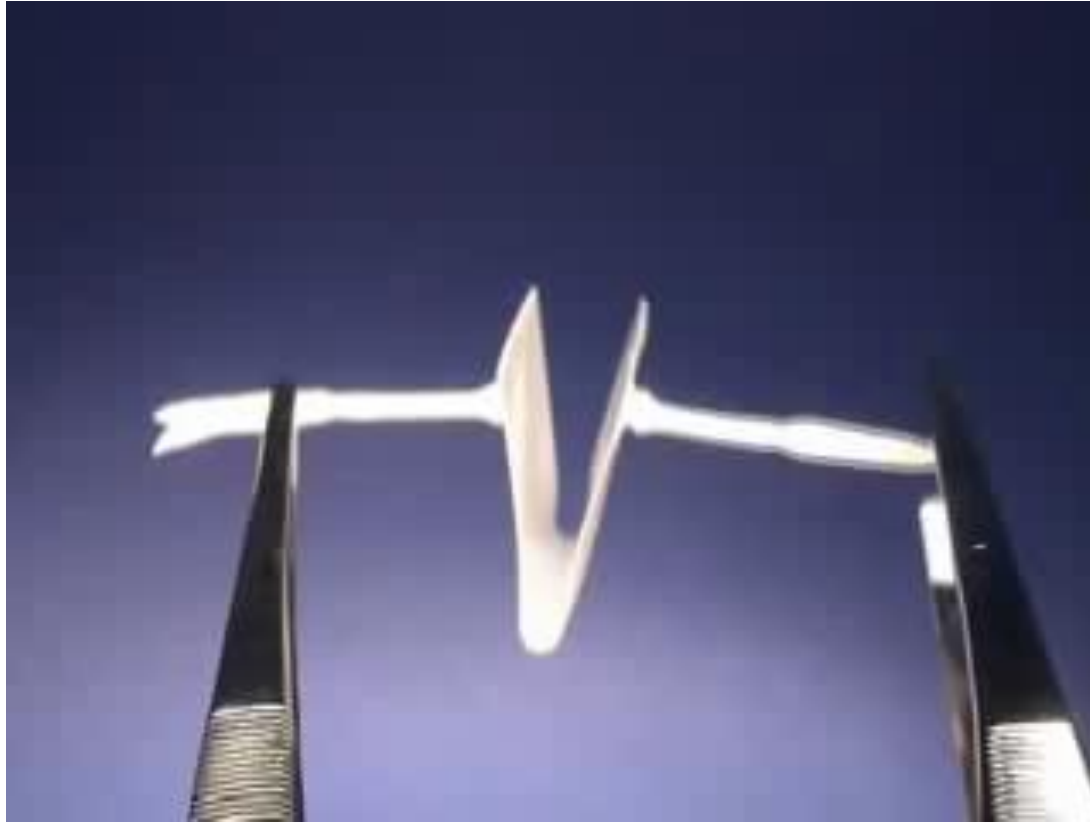


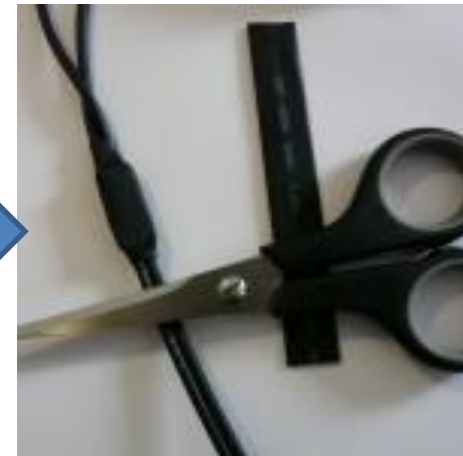
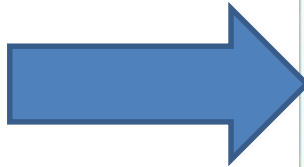




Alakemlékező polimerek







<https://fejhallgatoszerviz.hu/sony-dr-ga100-headset-javitasa-kabelcsere/>

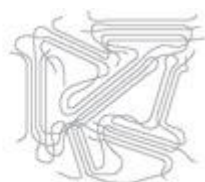
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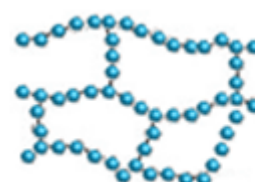
Szerkezet és átmeneti hőmérsékletek



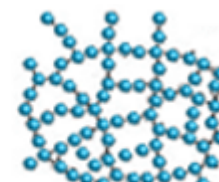
PVC, PS, PC, PMMA, SAN



PE, PP, PA, POM, PET, PBT



SBR, NR, BR; NBR

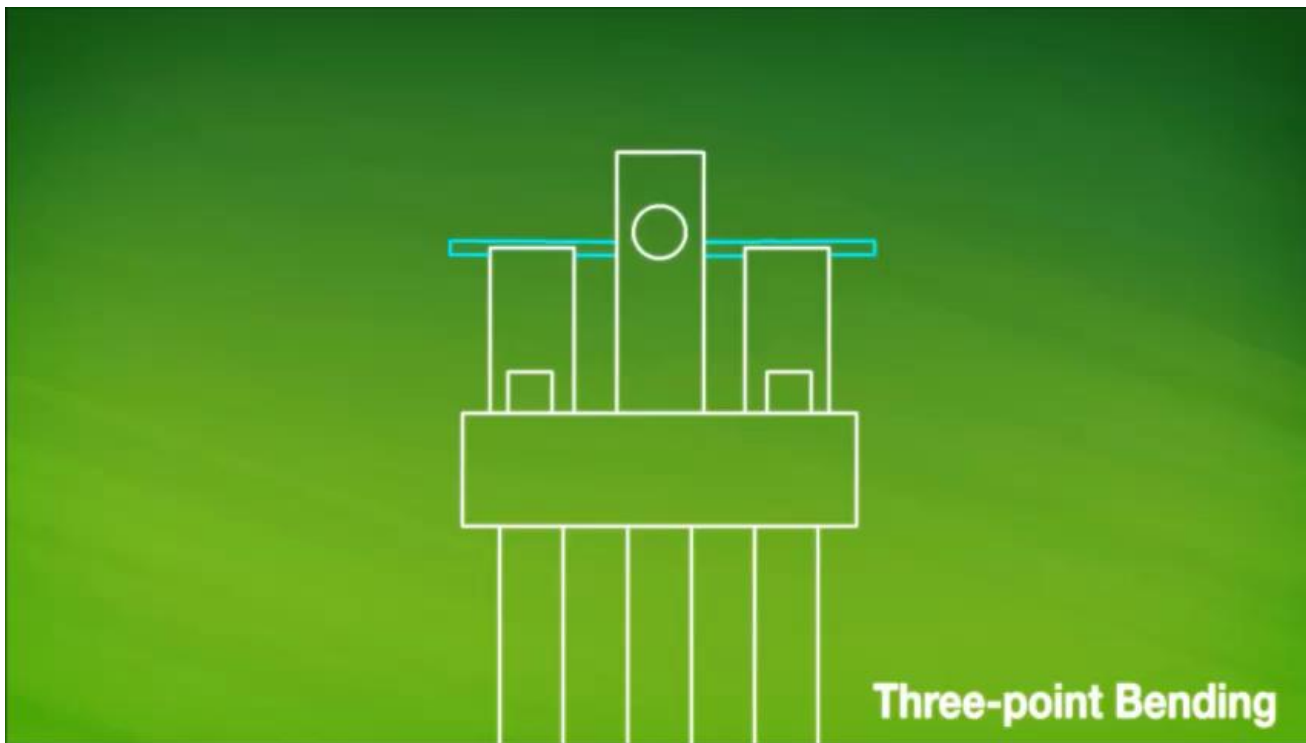


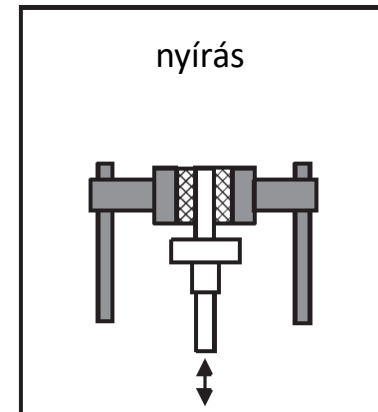
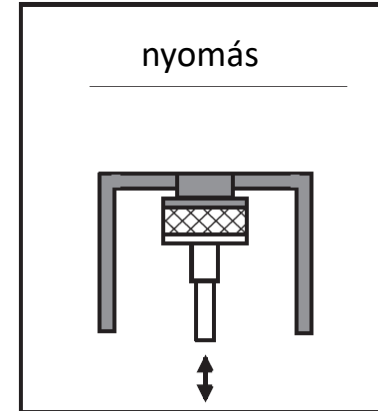
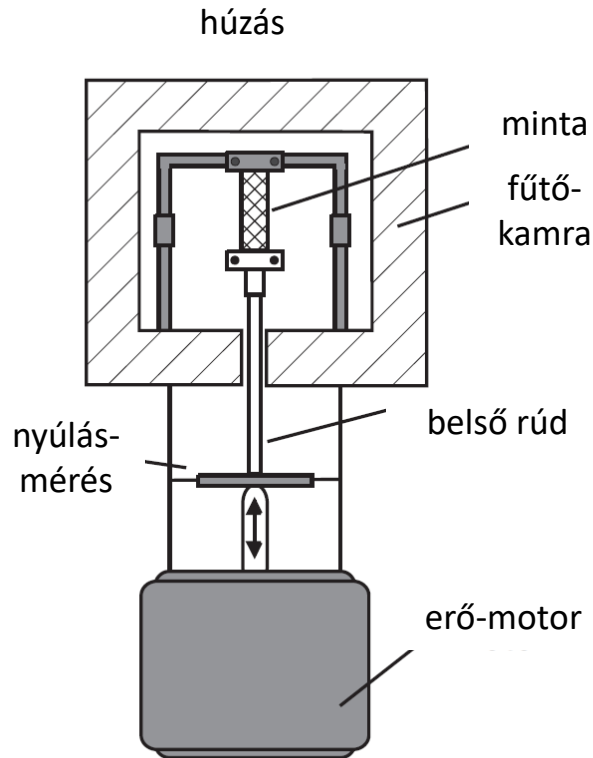
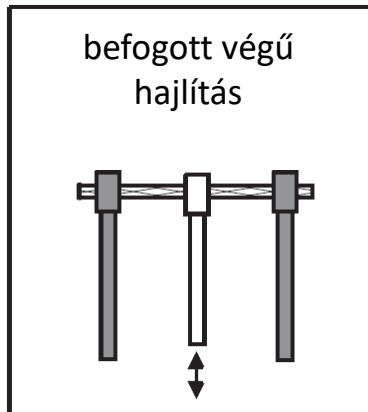
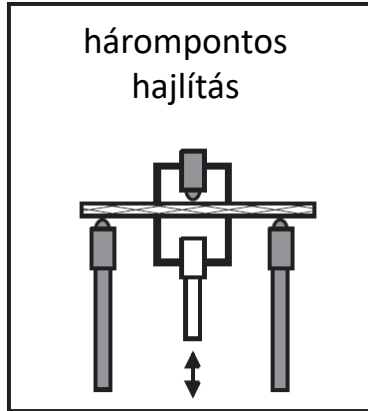
UP; VE; EP

ATP	0 K	⇒	T_g	⇒	T_f	⇒	T_b
GTE	0 K	⇒	T_g	⇒	⇒	⇒	T_b
STD	0 K	⇒	⇒	⇒	T_g	⇒	T_b
RK ($T_f < T_m$)	0 K	⇒	T_g	⇒	T_m	⇒	T_b



DMA görbék



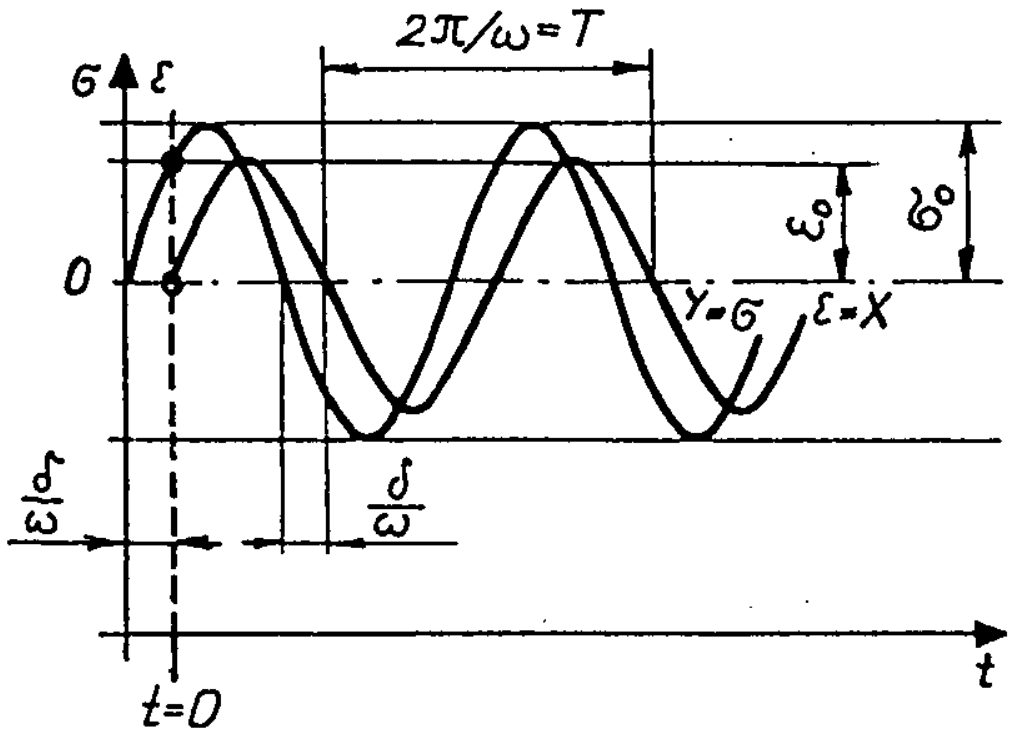


Gerjesztés:

$$\varepsilon(t) = \varepsilon_0 \sin \omega t$$

Válasz:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta)$$



Válasz: $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$

$$\sigma(t) = \sigma_0 \sin \omega t \cdot \cos \delta + \sigma_0 \cos \omega t \cdot \sin \delta$$

$$\sigma(t) = \underbrace{\sigma_0 \cos \delta}_{\sigma'_0} \cdot \sin \omega t + \underbrace{\sigma_0 \sin \delta}_{\sigma''_0} \cdot \cos \omega t$$

Gerjesztéssel
fázisban

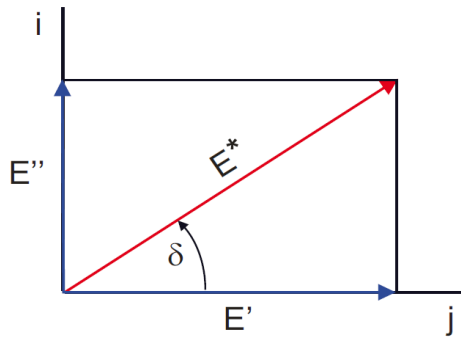
$\frac{\pi}{2}$ -vel eltolt

Tárolási
modulus

$$\frac{\sigma'_0}{\epsilon_0} = E'$$

$$\frac{\sigma''_0}{\epsilon_0} = E''$$

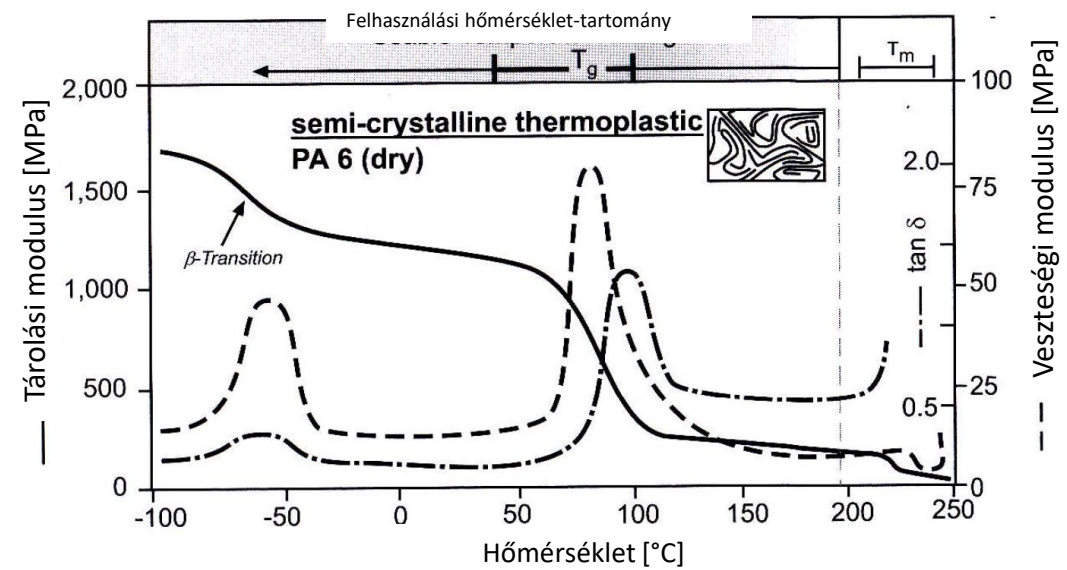
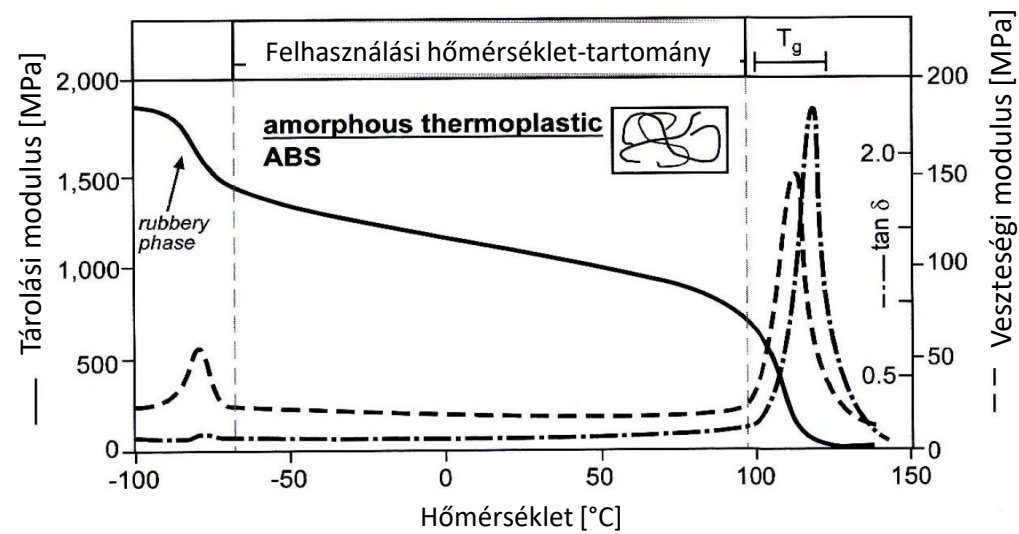
Veszteségi
modulus



$$d = \tan \delta = \frac{E''}{E'}$$

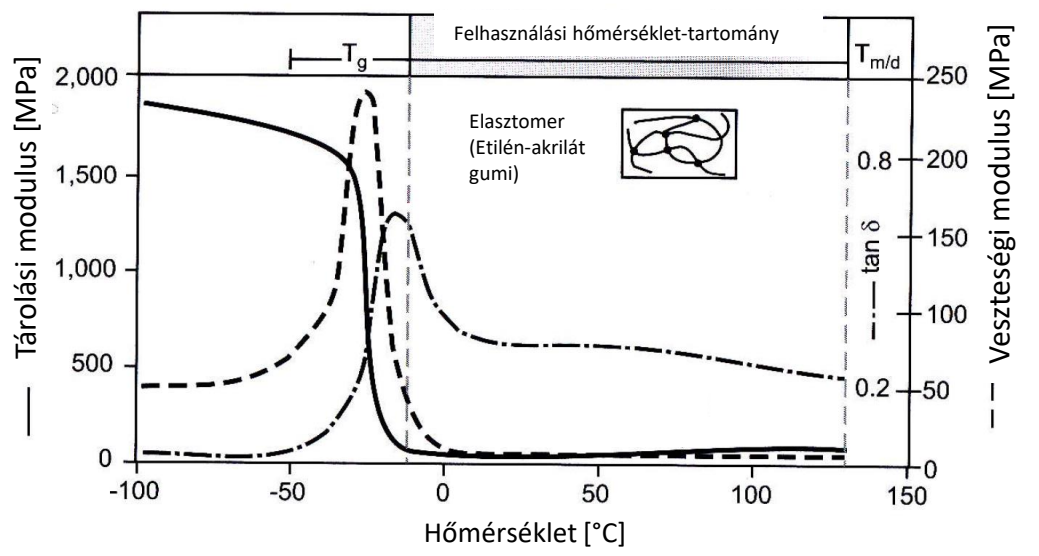
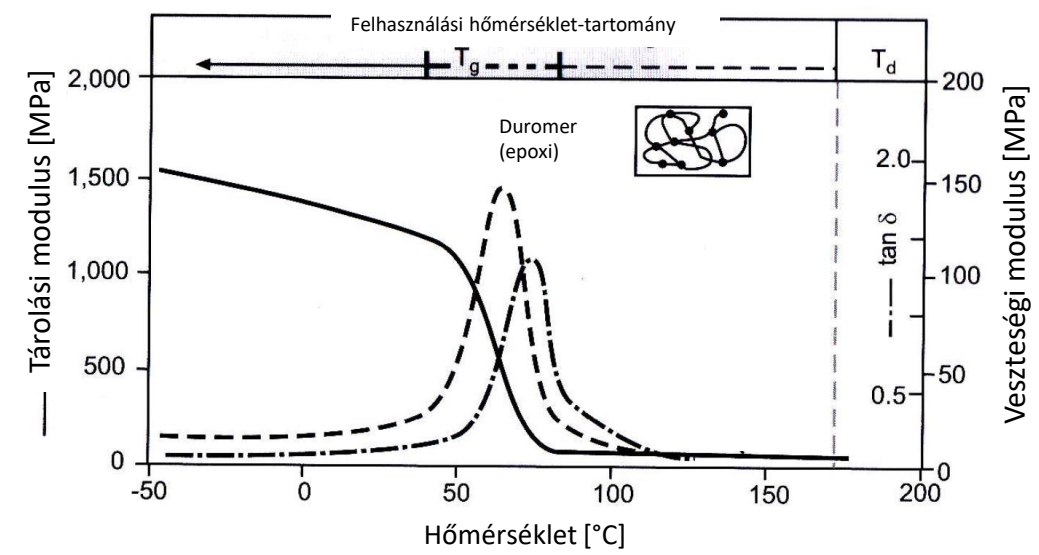


DMA görbék





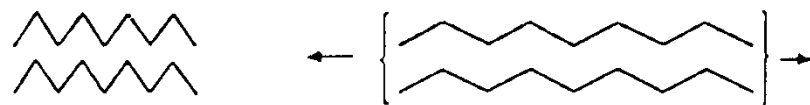
DMA görbék



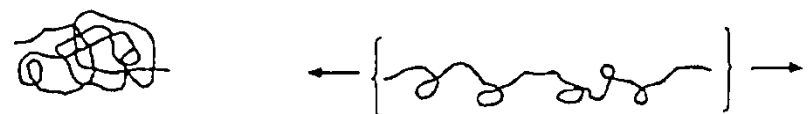


Mikrodeformáció komponensek

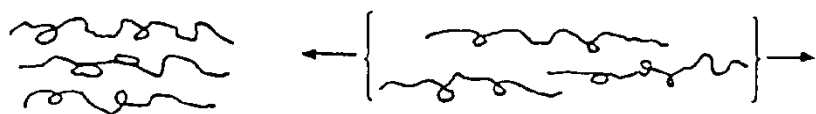
Energia rugalmas



Entrópiarugalmas



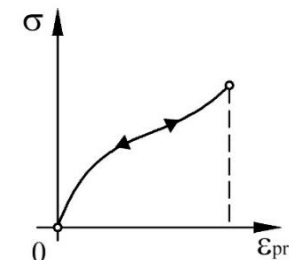
Energia disszipáló



Makrodeformáció komponensek

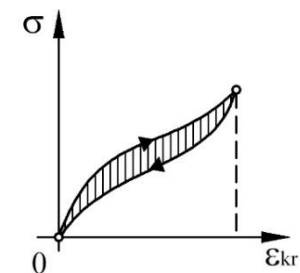
Pillanatnyi

rugalmas (ϵ_{pr})
(Mech: reverzibilis)
(Td: reverzibilis)



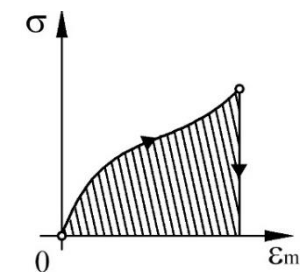
Késleltetett

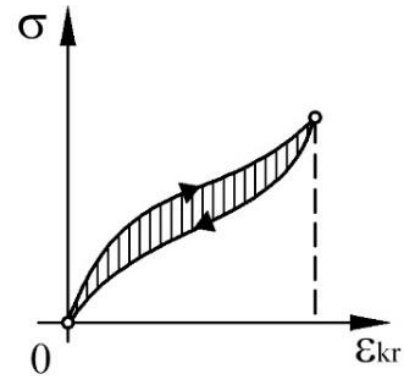
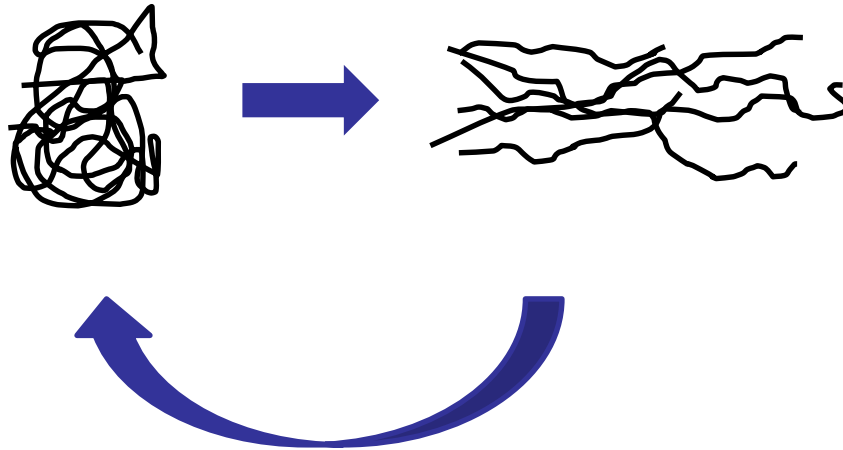
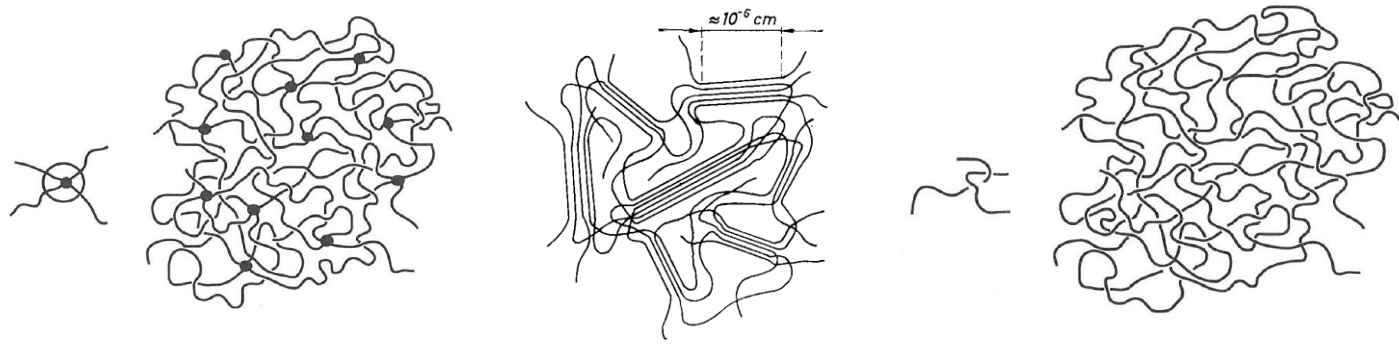
rugalmas (ϵ_{kr})
(Mech: reverzibilis)
(Td: irreverzibilis)



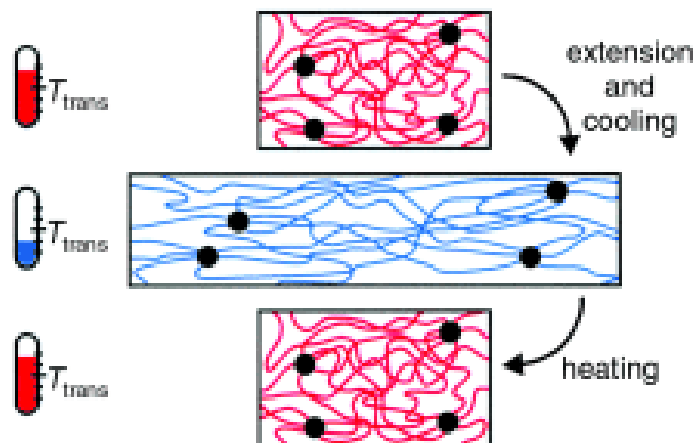
Maradó (ϵ_m)

(Mech: irrev.)
(Td: irreverzibilis)

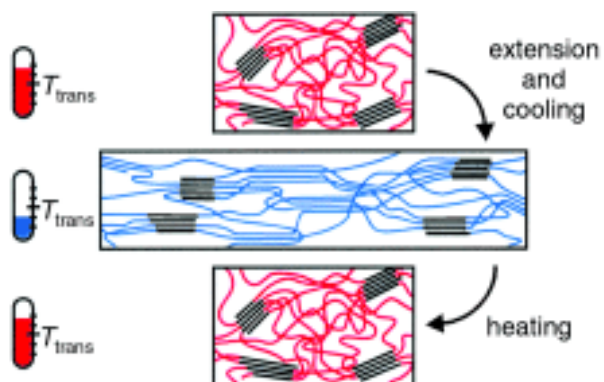




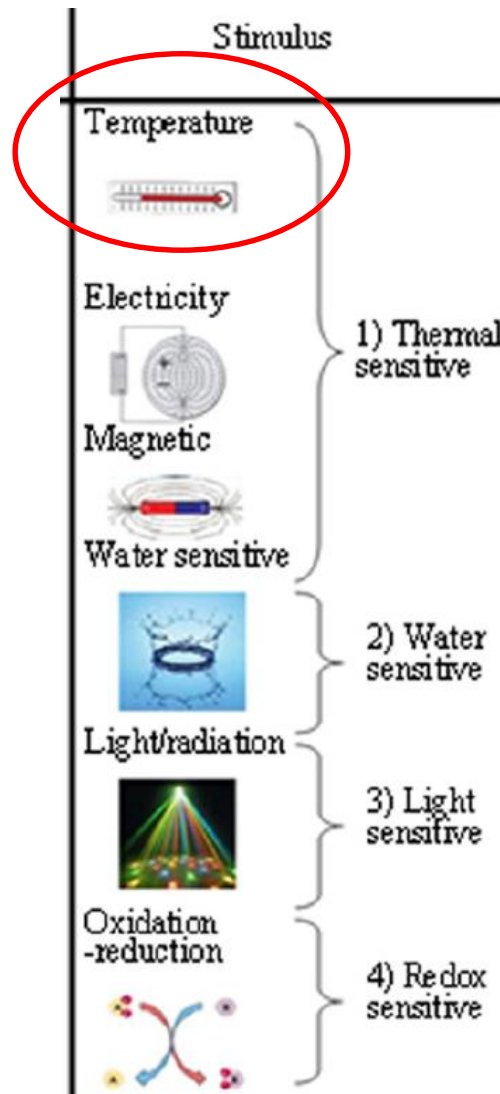
Polimerek alakemlékező mechanizmusa molekuláris szinten

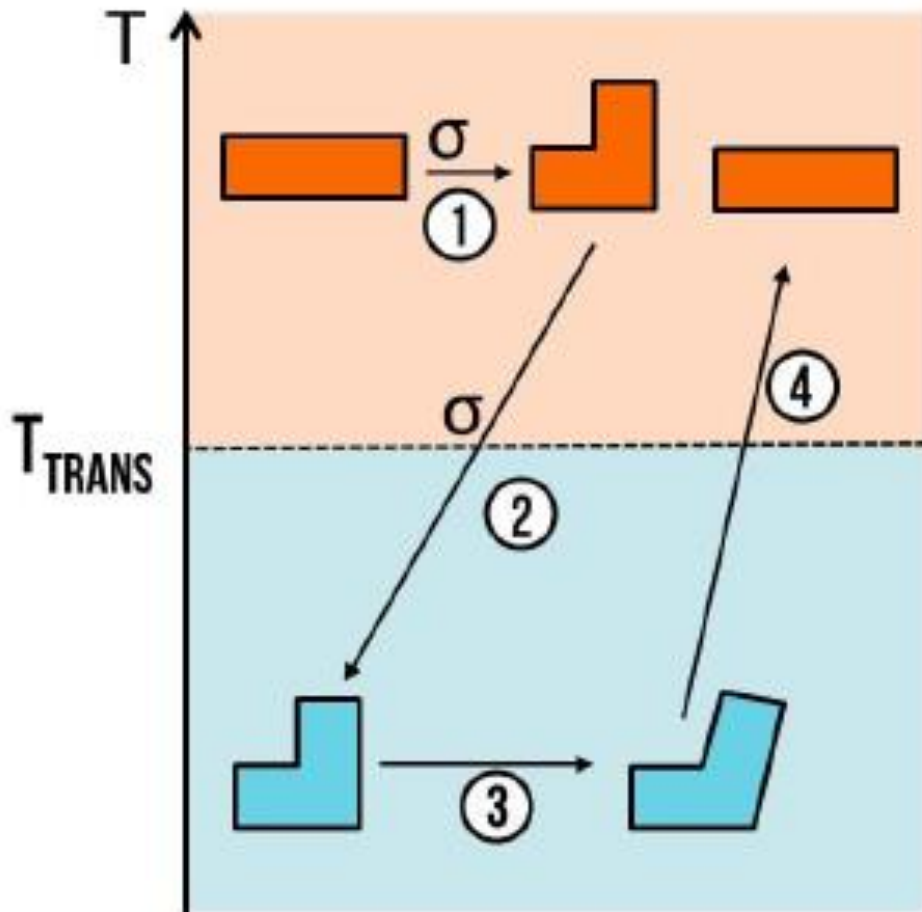


Polimerek alakemlékező mechanizmusa molekuláris szinten



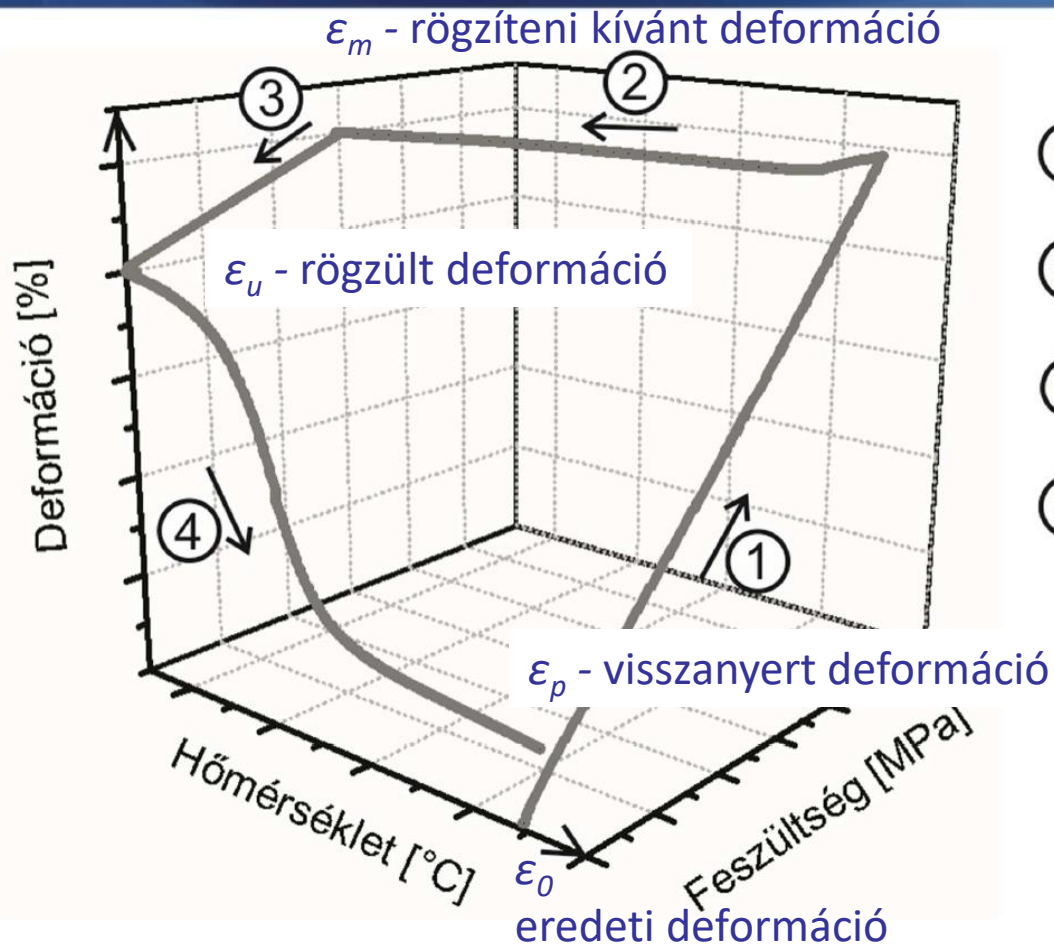
Alakemlékezést kiváltó ingerek



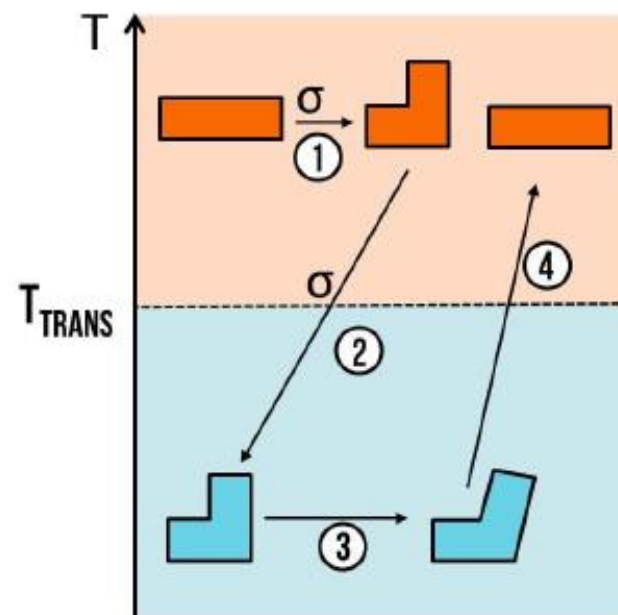


- ① Alakadás
- ② Alakrögzítés
- ③ Külső kényszer megszüntetése
- ④ Visszaalakulás

Szabad visszaalakulású alakemlékezési ciklus háromdimenziós ábrázolása



- ① Alakadás
- ② Alakrögzítés
- ③ Külső kényszer megszüntetése
- ④ Visszaalakulás

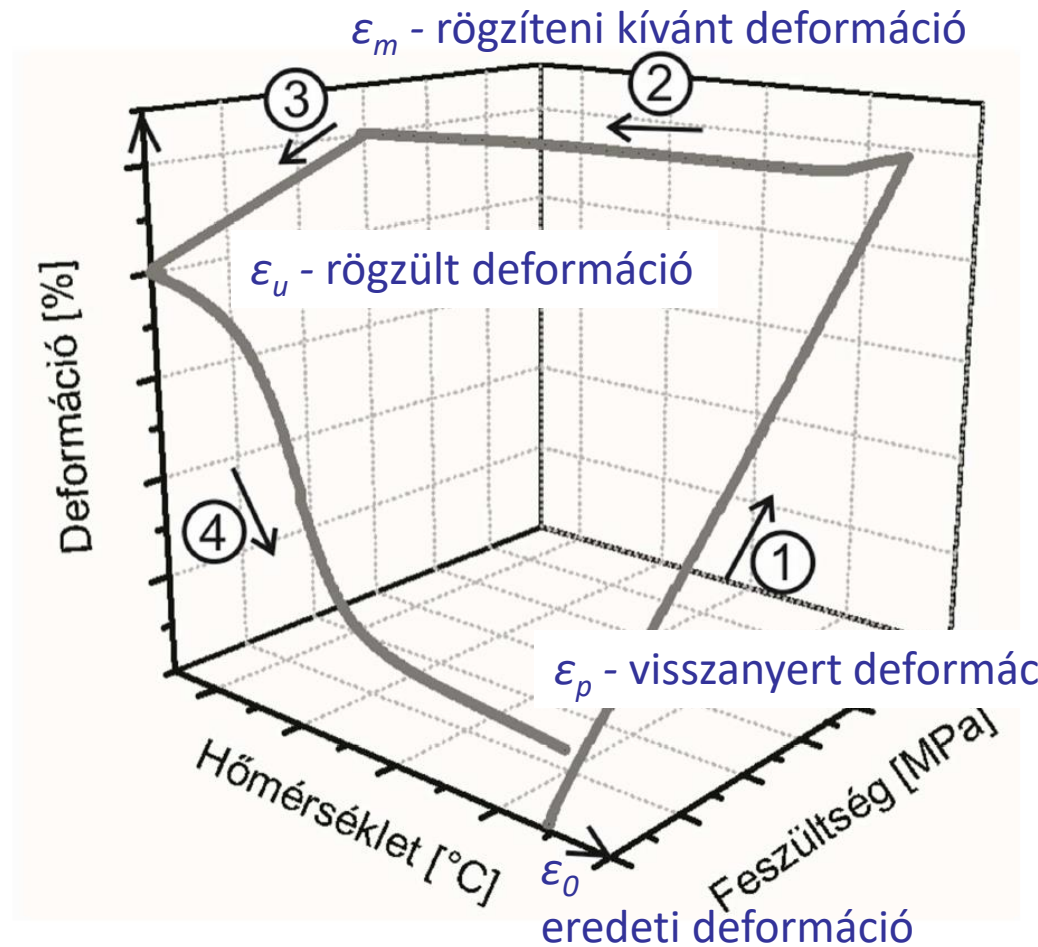


$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \cdot 100$$



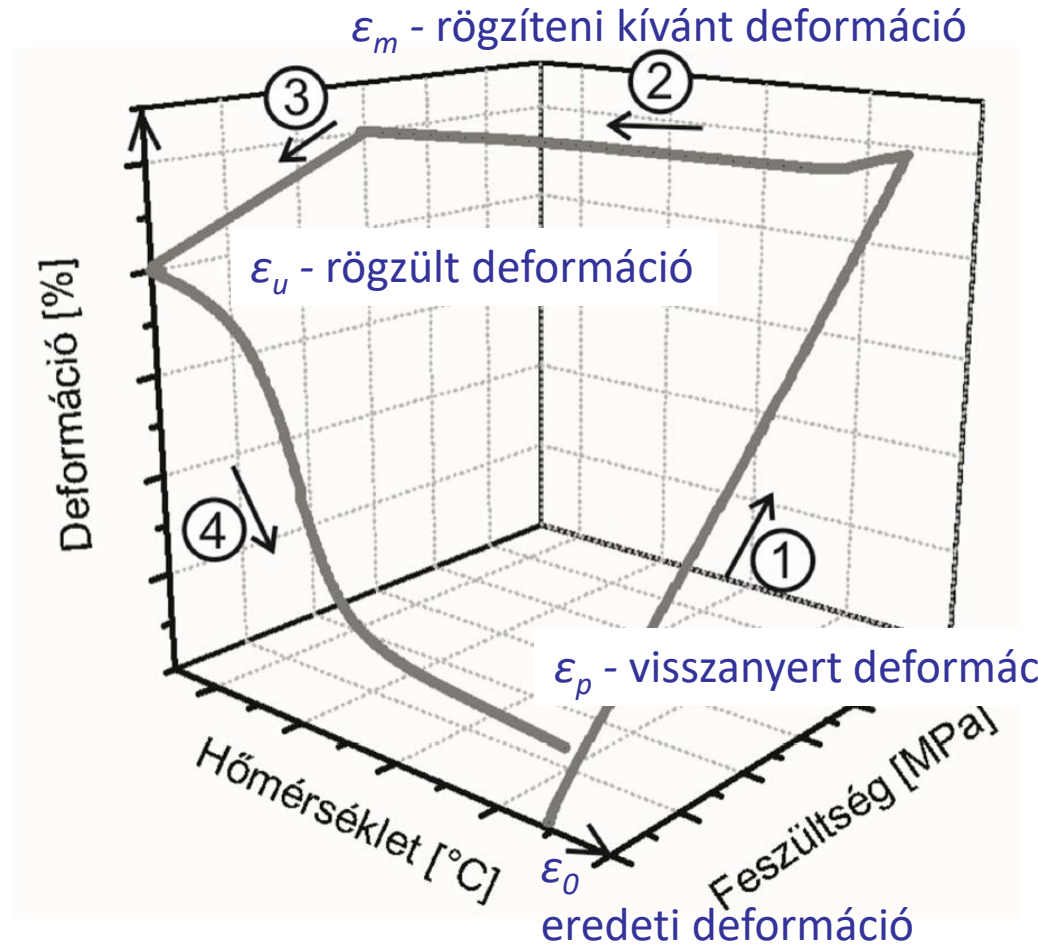
R_f - alakrögzítési tényező; ε_m - rögzíteni kívánt deformáció, ε_u - rögzült deformáció

$$R_r = \frac{\overset{\text{visszanyert}}{\varepsilon_m - \varepsilon_p}}{\underset{\text{eredeti}}{\varepsilon_m - \varepsilon_0}} \cdot 100$$



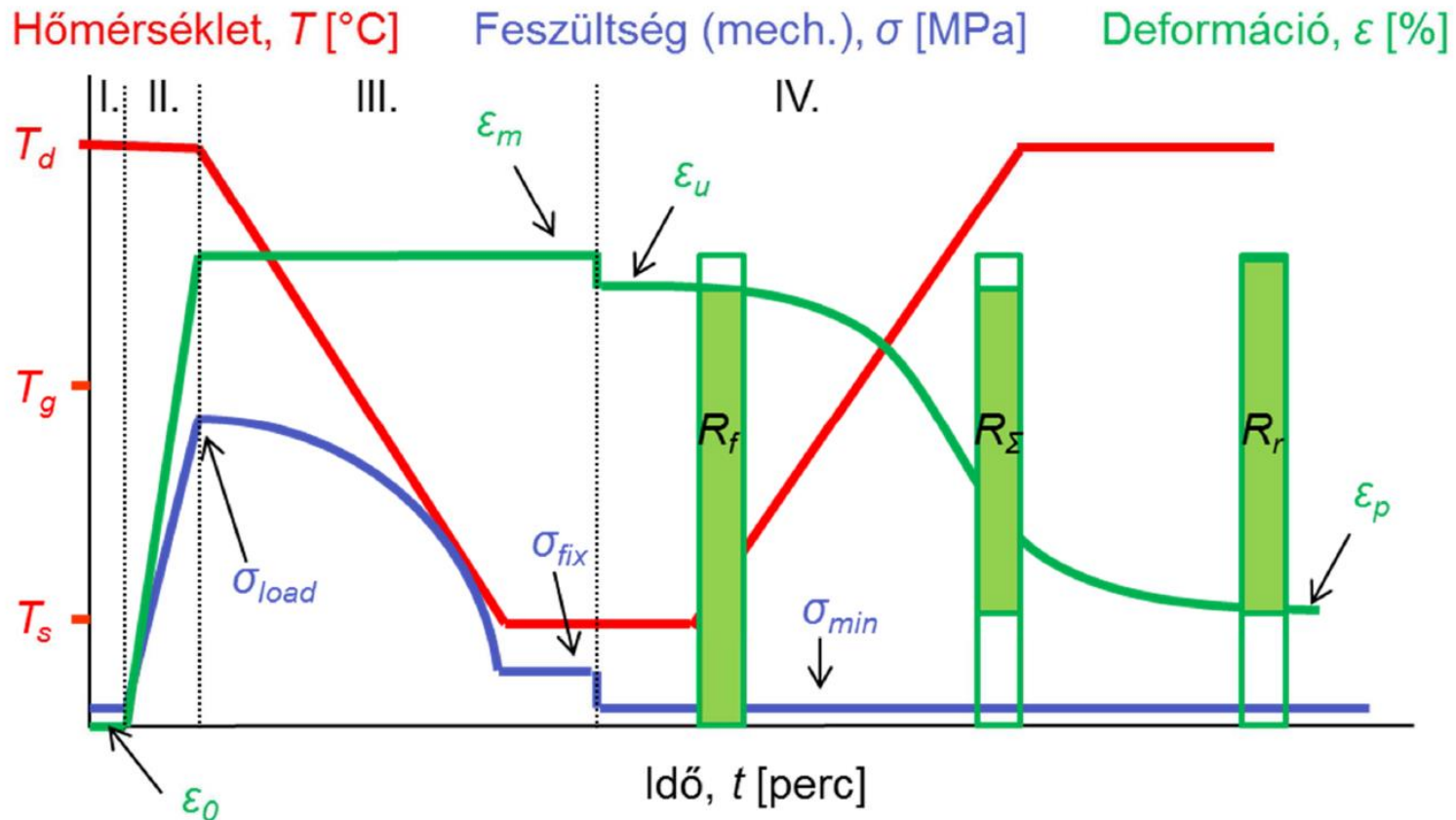
R_r - visszaalakulási tényező

$$R_{\Sigma} = \frac{\overset{\text{megvalósult}}{\varepsilon_u - \varepsilon_p}}{\underset{\text{elméleti max.}}{\varepsilon_m - \varepsilon_0}} \cdot 100$$

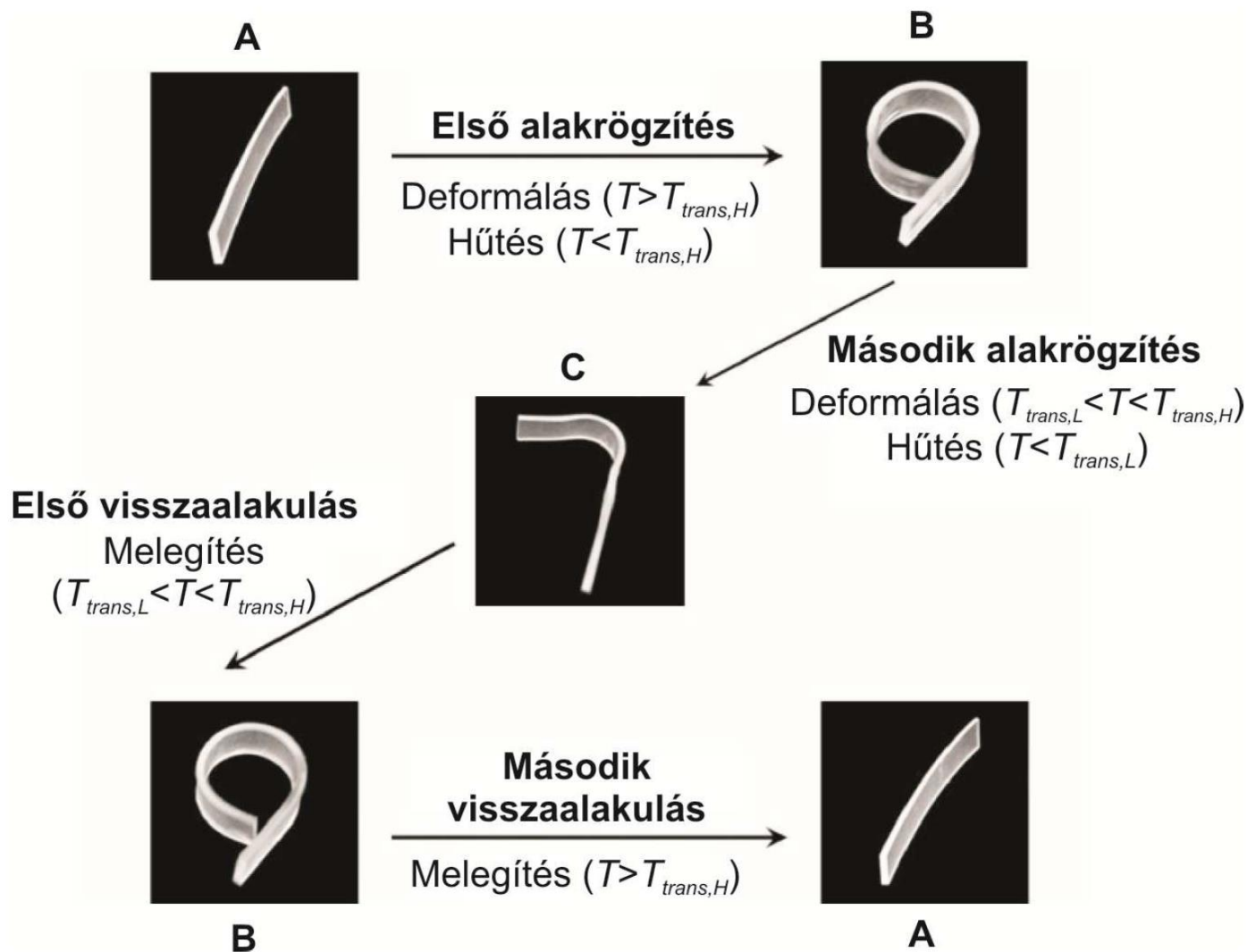


R_{Σ} - összesített alakemlékezési tényező

Egy alakemlékező vizsgálat mérési ciklusa



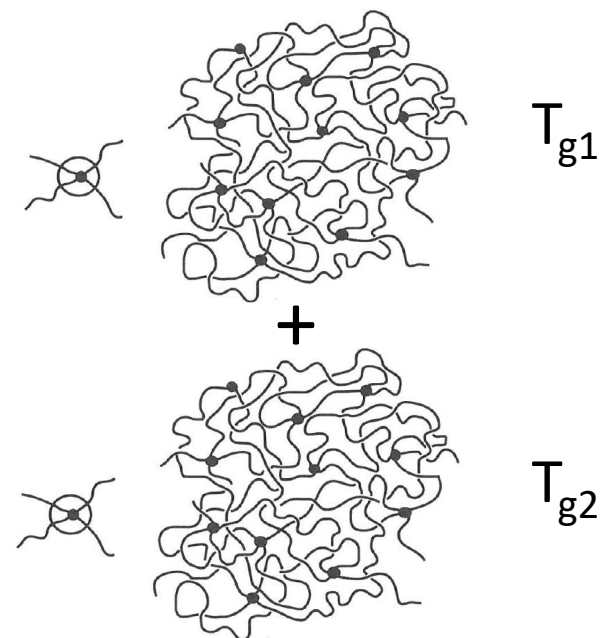
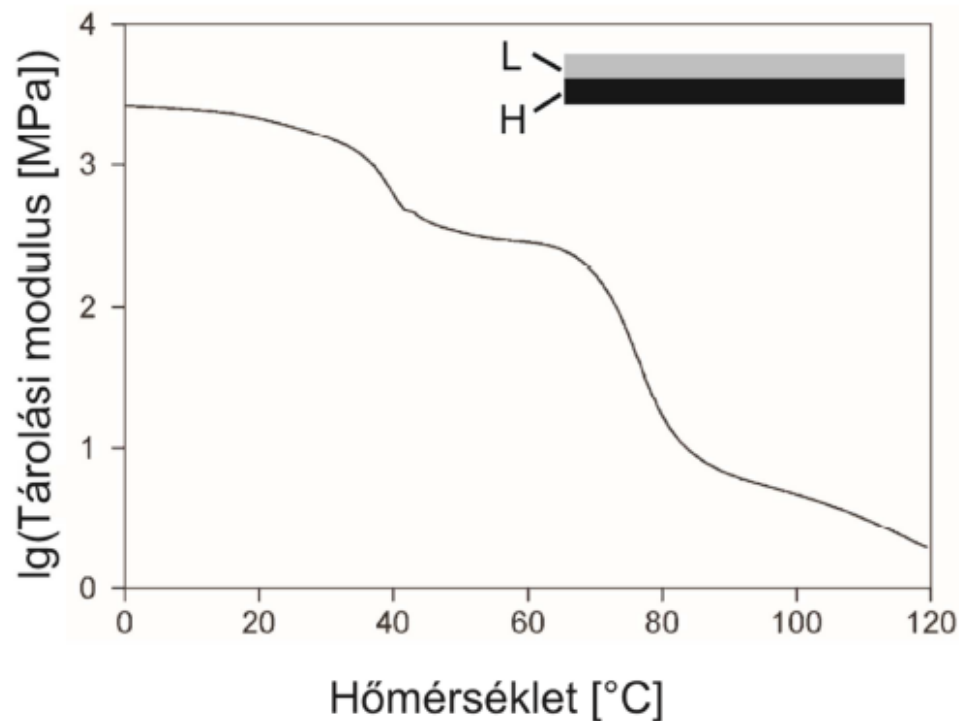
I. felfűtés és hőntartás, II. alakadás, III. alakrögzítés, IV. újramelegítés (szabad visszaalakulással), T_s tárolási hőmérséklet, T_g üveges átmeneti hőmérséklet, T_d alakadási hőmérséklet, σ_{min} visszaalakulási feszültség, σ_{load} alakadási feszültség, σ_{fix} alakrögzítési feszültség, ε_0 eredeti deformáció, ε_m rögzített deformáció, ε_u rögzült deformáció, ε_p visszanyert deformáció, R_f alakrögzítési tényező, R_r visszaalakulási tényező, R_Σ összesített alakemlékezési tényező.



Xie T., Xiao X., Cheng Y-T.: Revealing triple-shape memory effect by polymer bilayers. *Macromolecular Rapid Communications*, 30, 1823-1827 (2009).



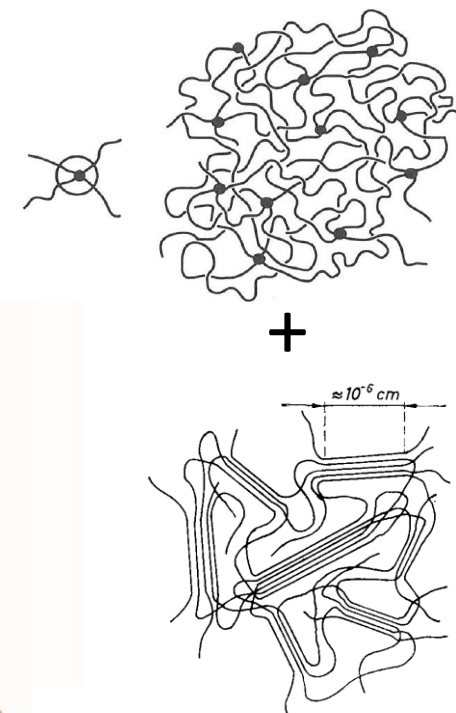
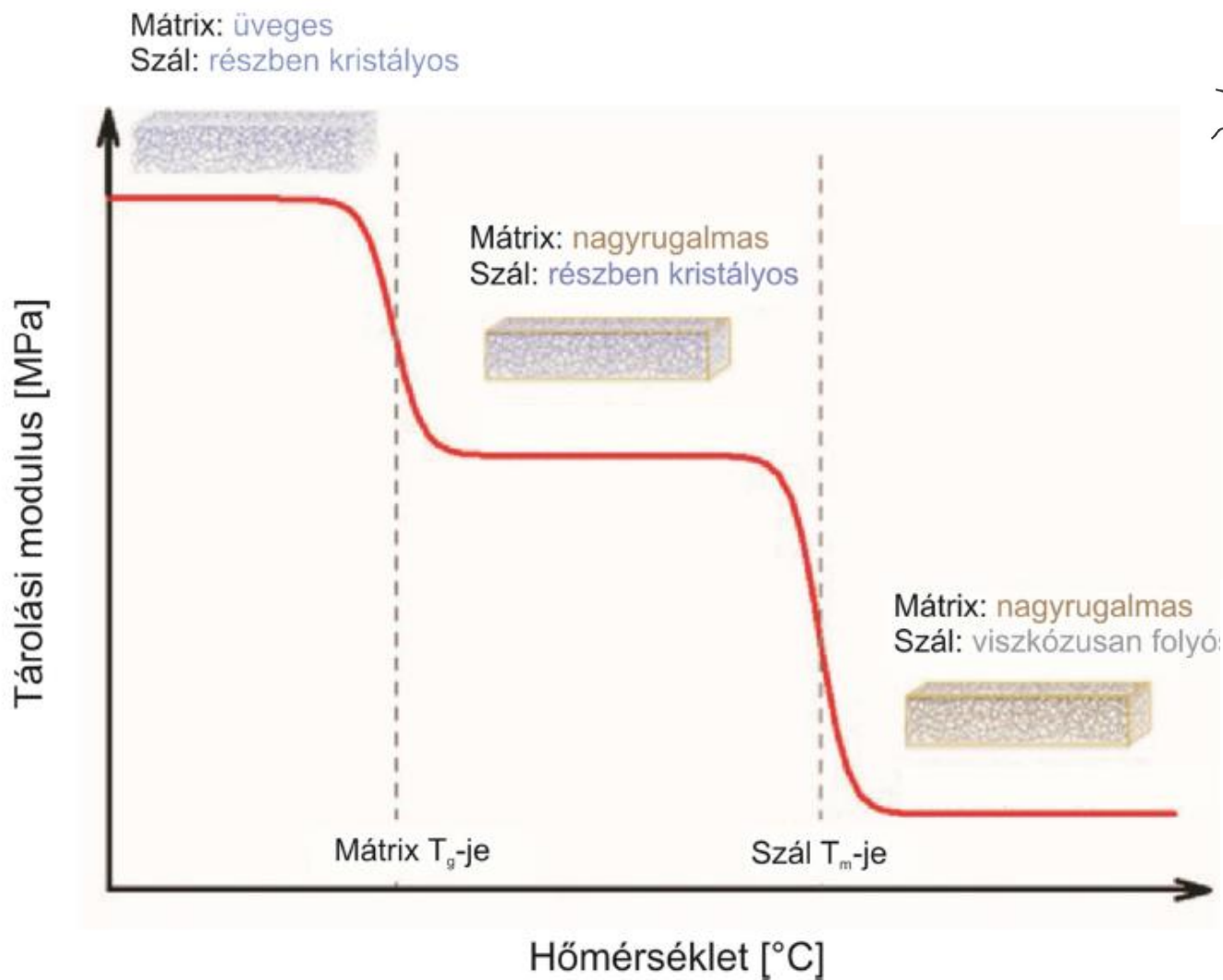
Két alakra emlékezés

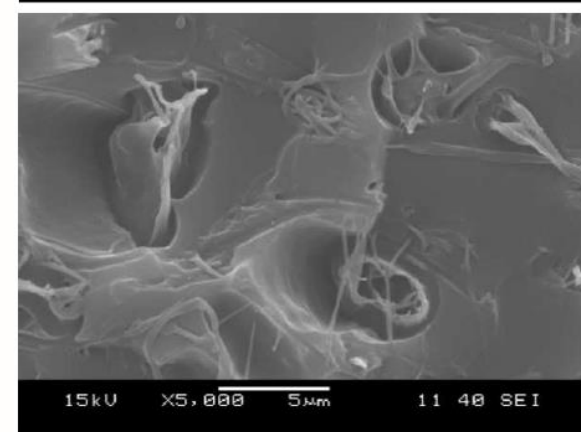
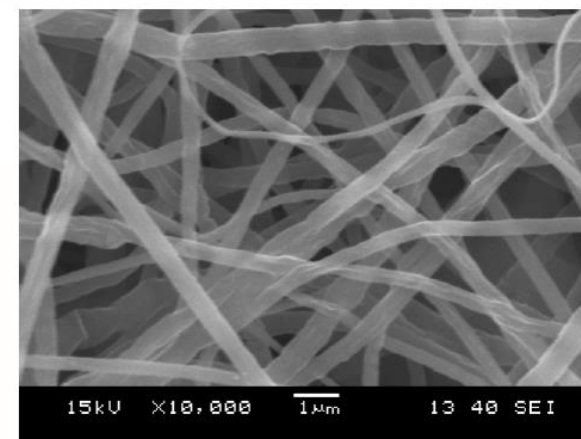
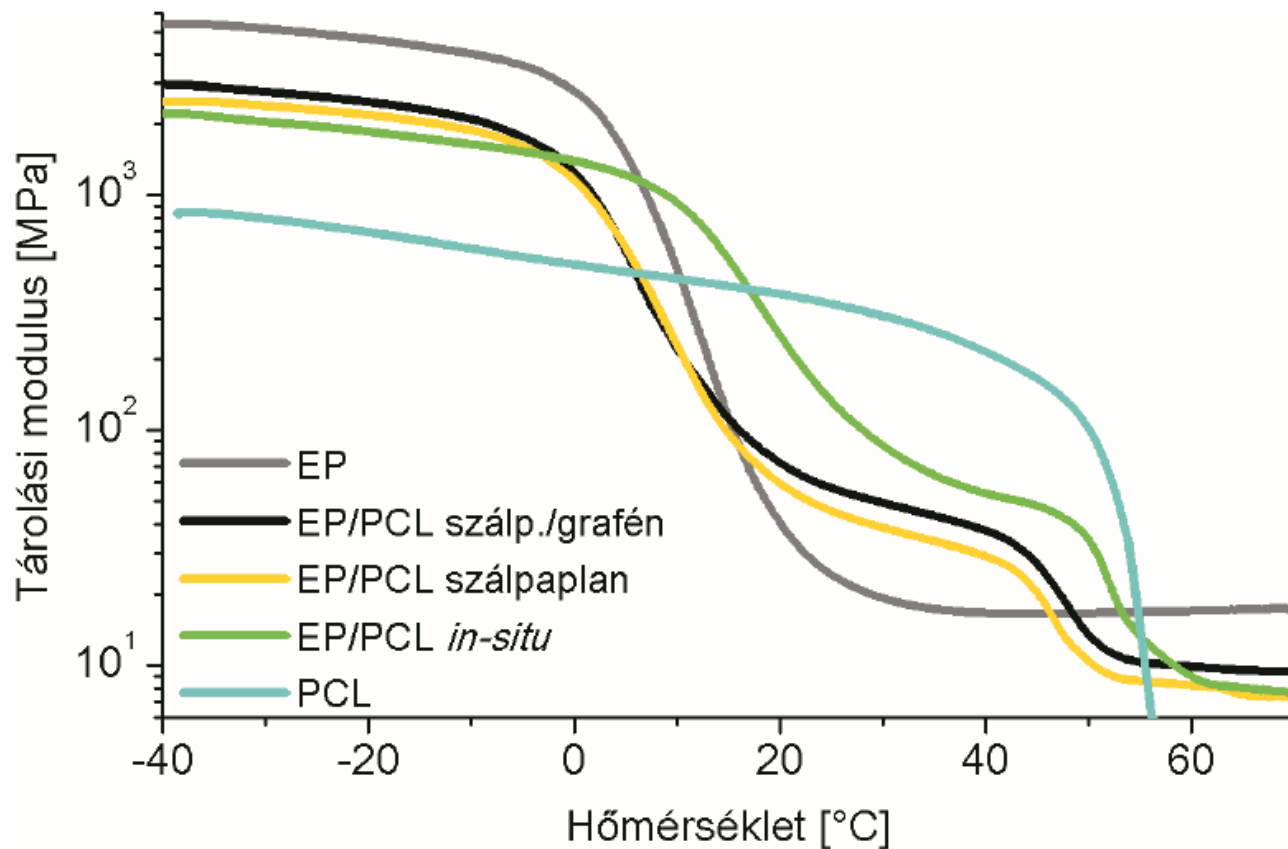


Xie T., Xiao X., Cheng Y-T.: Revealing triple-shape memory effect by polymer bilayers. *Macromolecular Rapid Communications*, 30, 1823-1827 (2009).



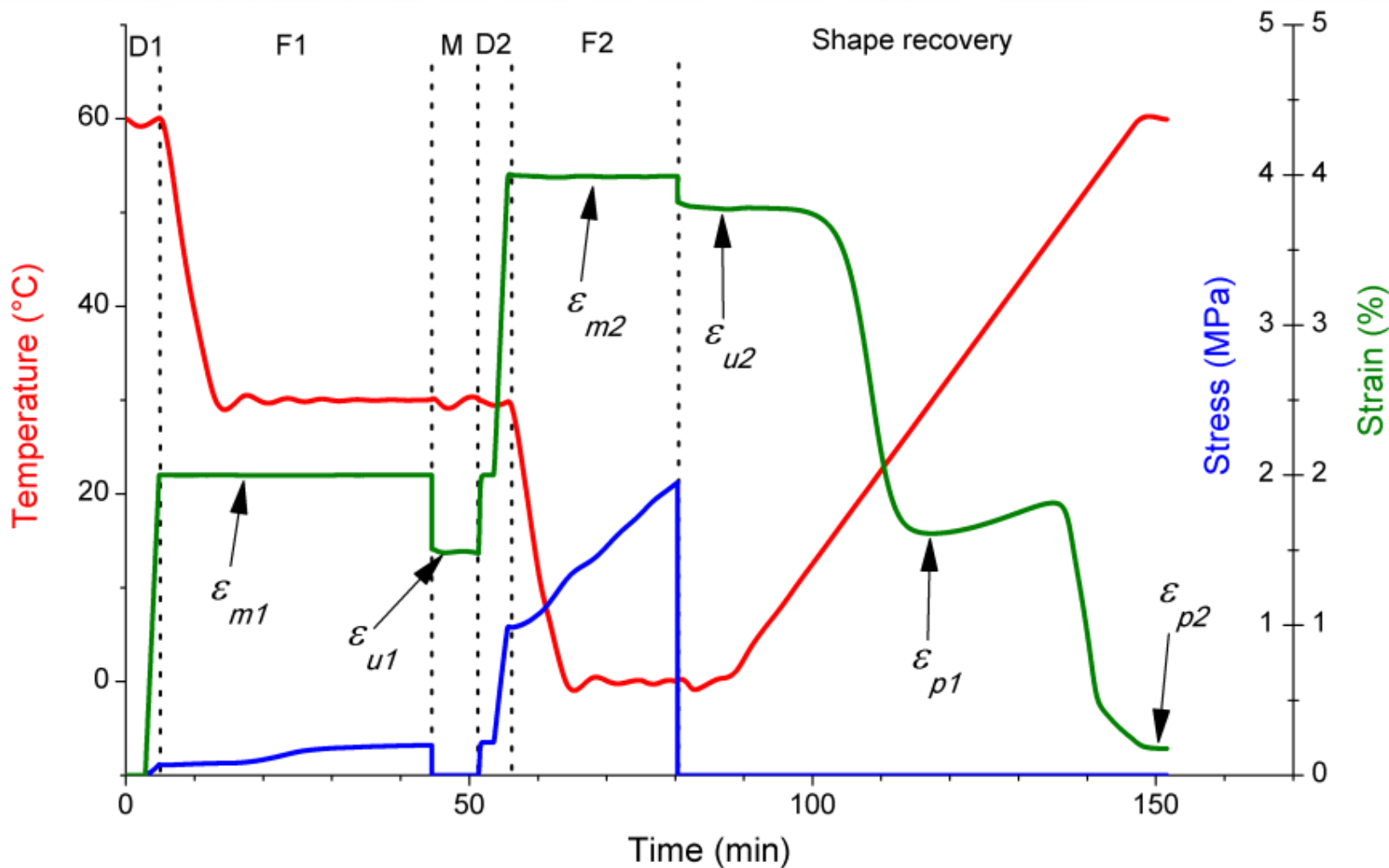
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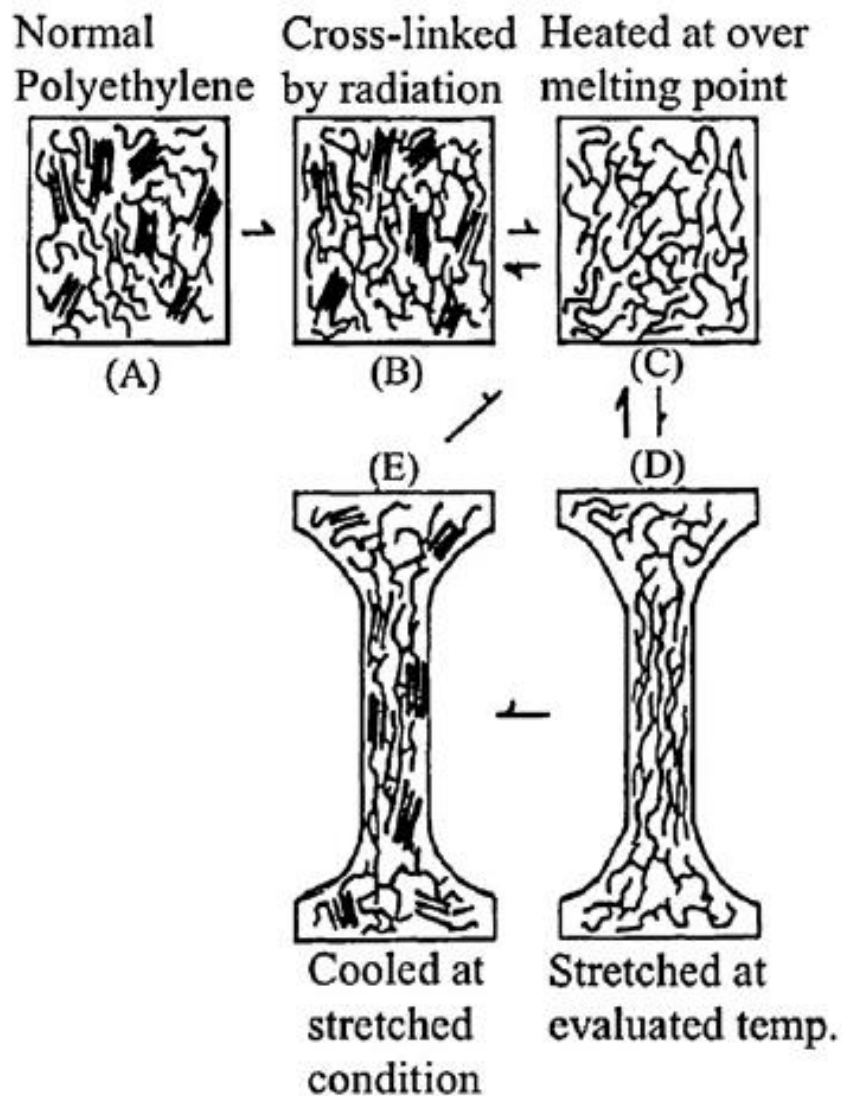
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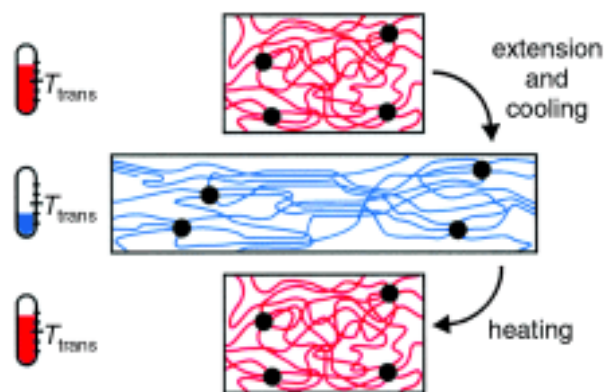
Fejős M., Molnár K., Karger-Kocsis J.: Epoxy/Polycaprolactone Systems with Triple-Shape Memory Effect: Electrospun Nanoweb with and without Graphene Versus Co-Continuous Morphology. *Materials*, 6 (2013) 4489-4504.



Két alakra emlékezés

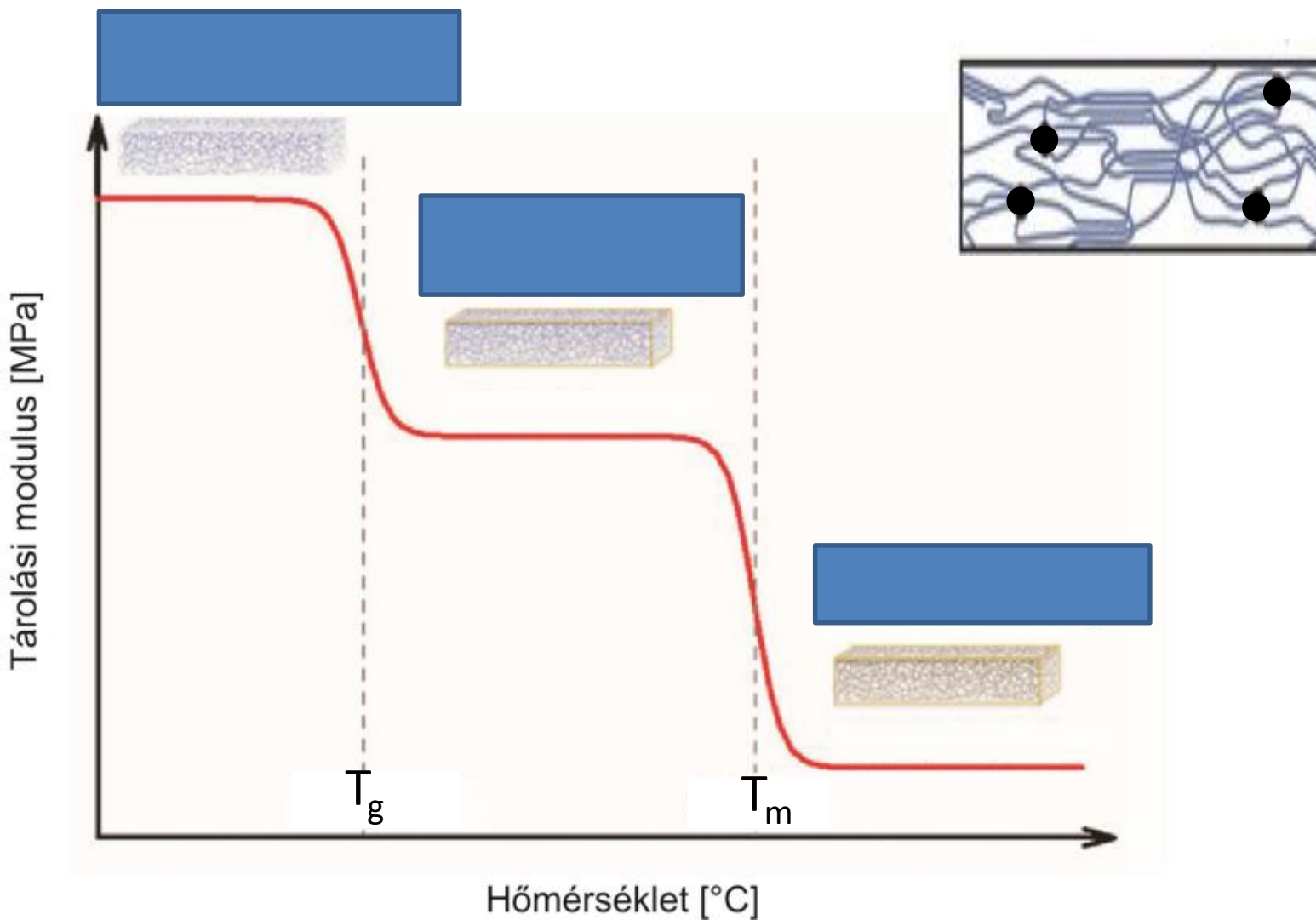


Polimerek alakemlékező mechanizmusa molekuláris szinten





Két alakra emlékezés



Fejős Márta – PhD értekezés alapján

Behl M., Lendlein A.: Shape-memory polymers. *Materials Today*, 10 (2007) 20-28.

A gyapjú mint alakemlékező polimer

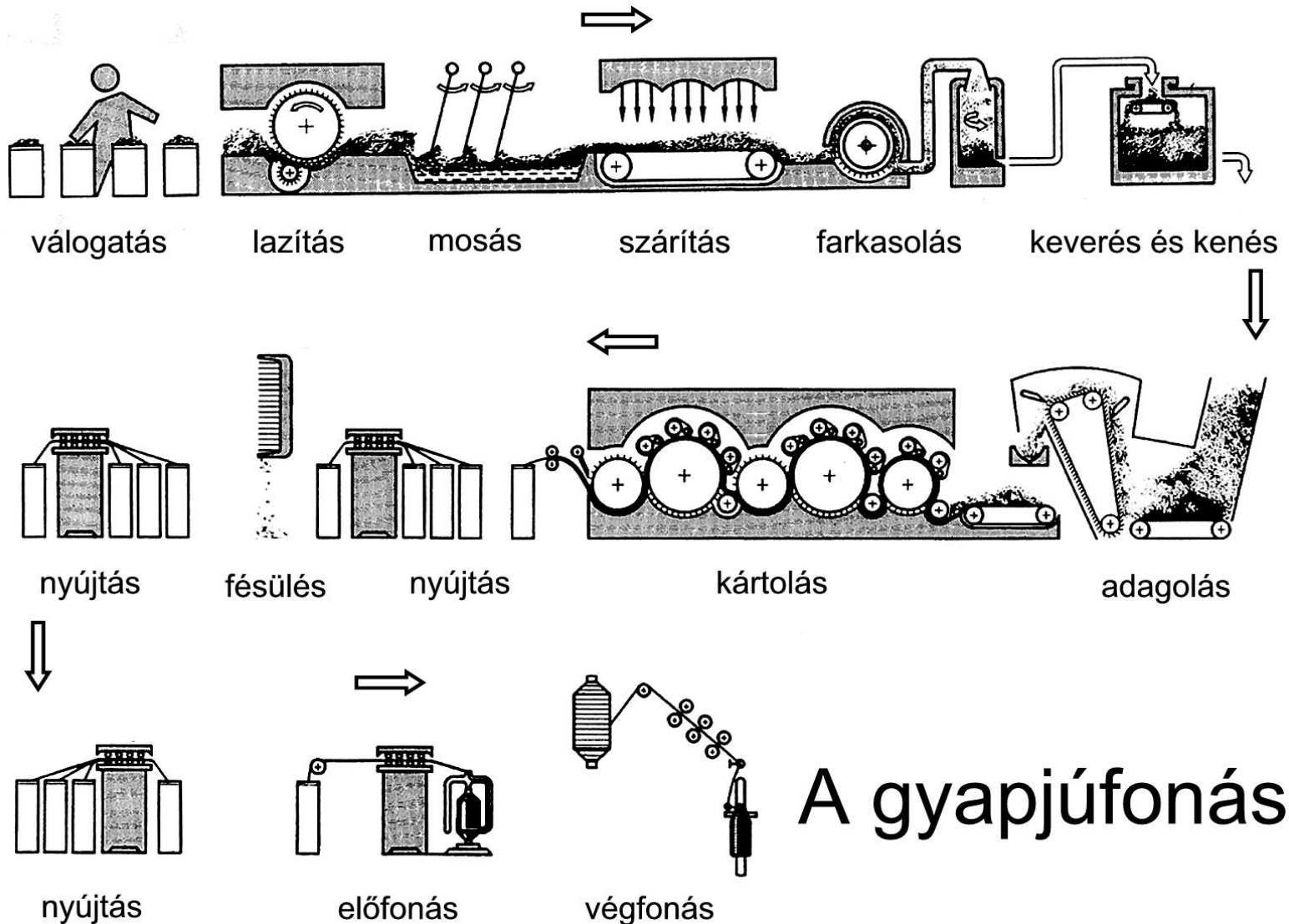


http://www.behir.hu/sites/default/files/field/image/birka_0.jpg



http://www.hkrita.com/html/upload/1317008643303_wool%20garment_U%20and%20treated.JPG

A gyapjú mint alakemlékező polimer

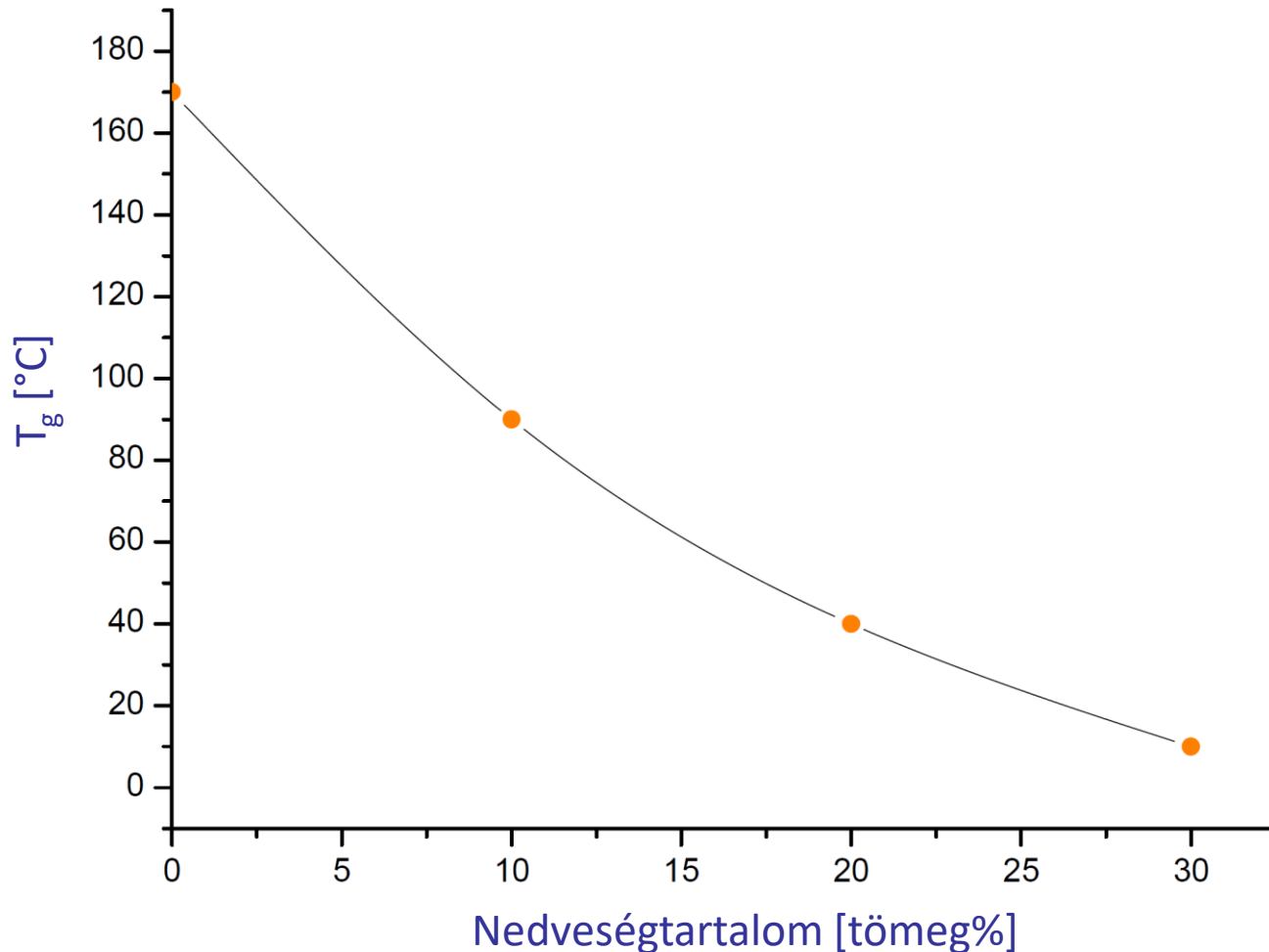


A gyapjúfonás

A gyapjú mint alakemlékező polimer



A gyapjú mint alakemlékező polimer



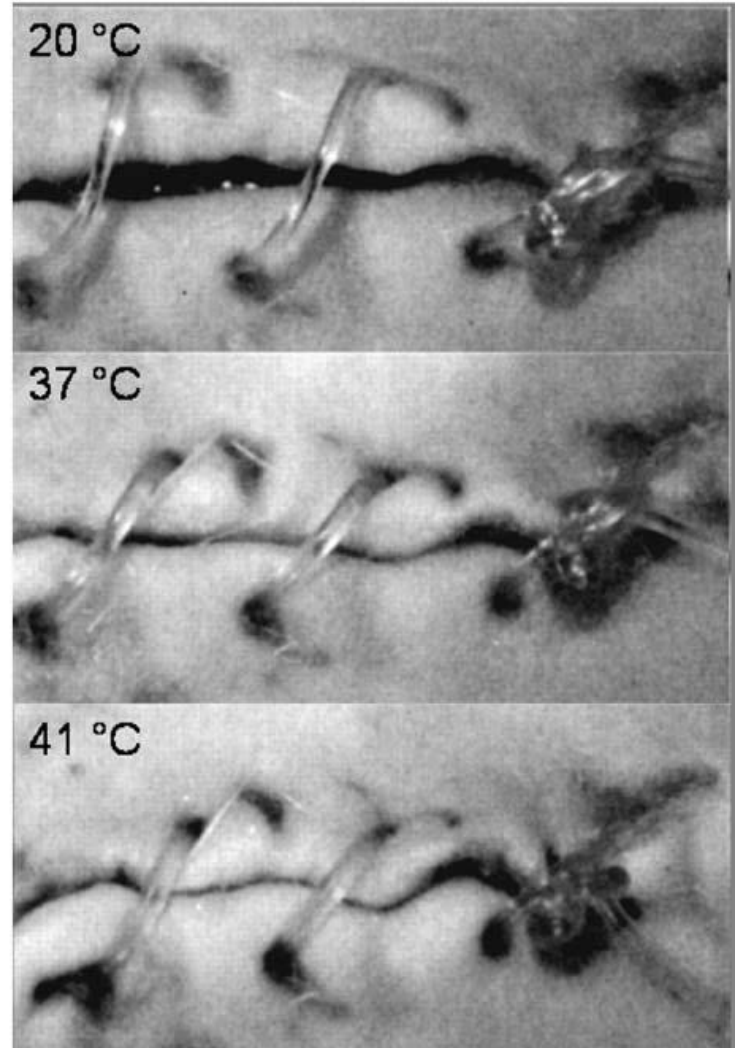
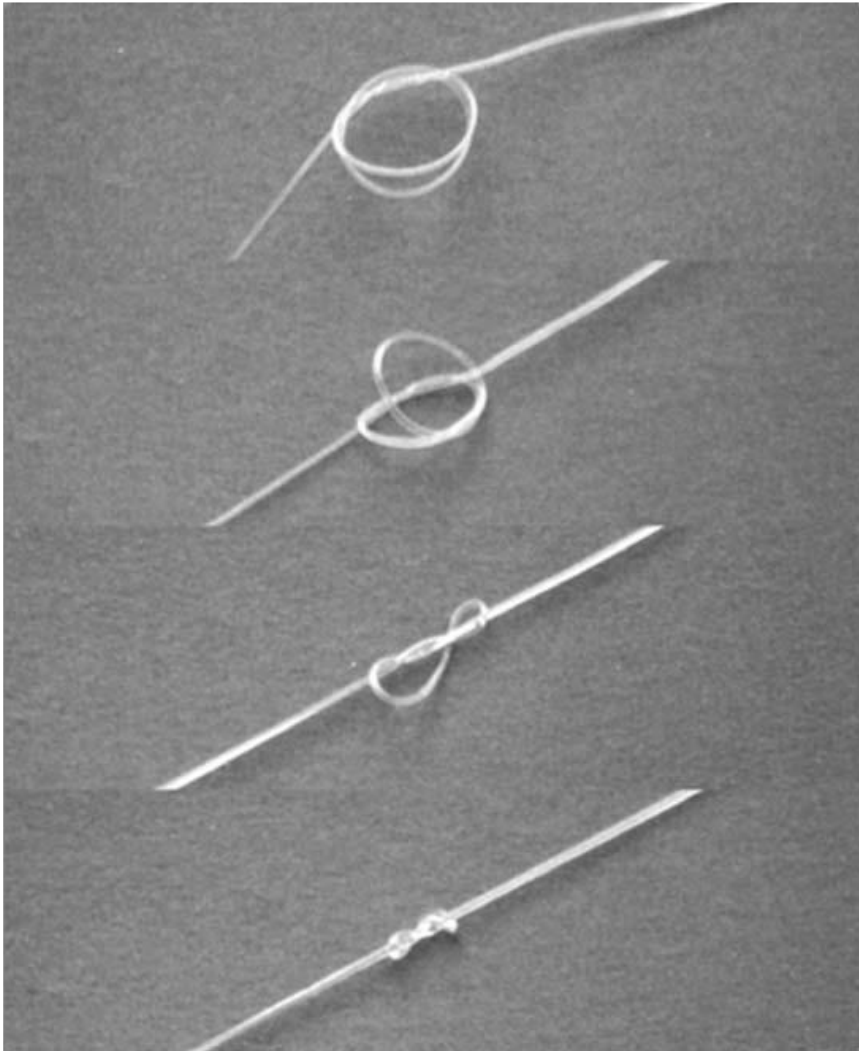
Hu J., Dong Z.-E., Liu Y., Liu Y.: The Investigation about the shape memory behavior of wool, *Advances in Science and Technology*, 60 (2008) 1-10.



Egy reflektor ideiglenes (balra) és visszanyert (jobbra) alakjában

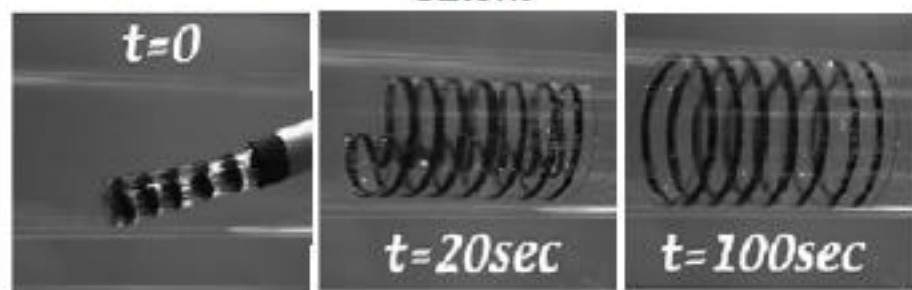


Leng J., Lan X., Liu Y., Du S.: Shape-memory polymers and their composites: Stimulus methods and applications. Progress in Materials Science, 56, 1077-1135 (2011).



Orvostechnika

Szent



C. M. Yakacki et al.: Biomaterials 28, 2007, 2255-2263

Az alakemlékezés mindig jó nekünk?





BUDAPESTI MŰSZAKI ÉS
GAZDASÁGTUDOMÁNYI EGYETEM
GÉPÉSZMÉRNÖKI KAR

POLIMERTECHNIKA
TANSZÉK

