What can gummy bears teach us about biological elastomers?

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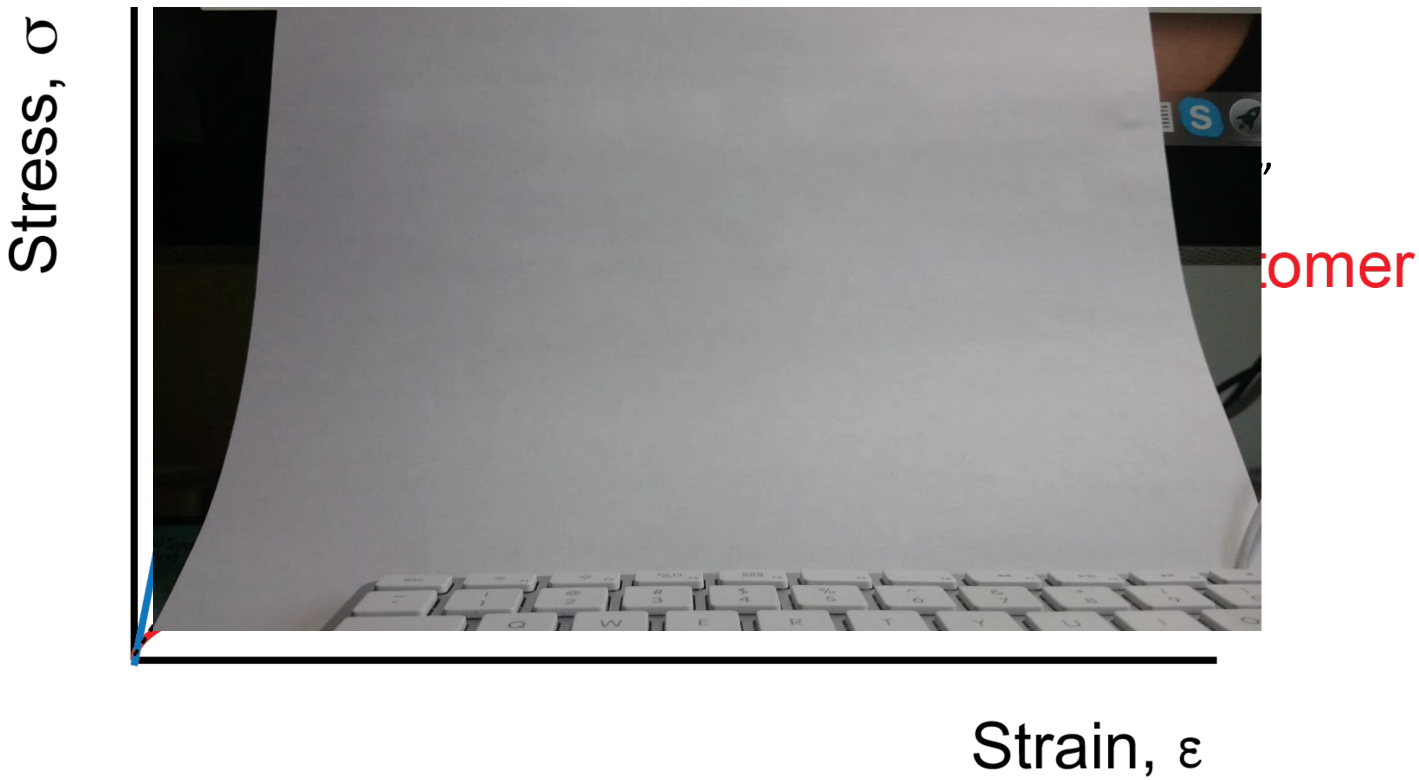
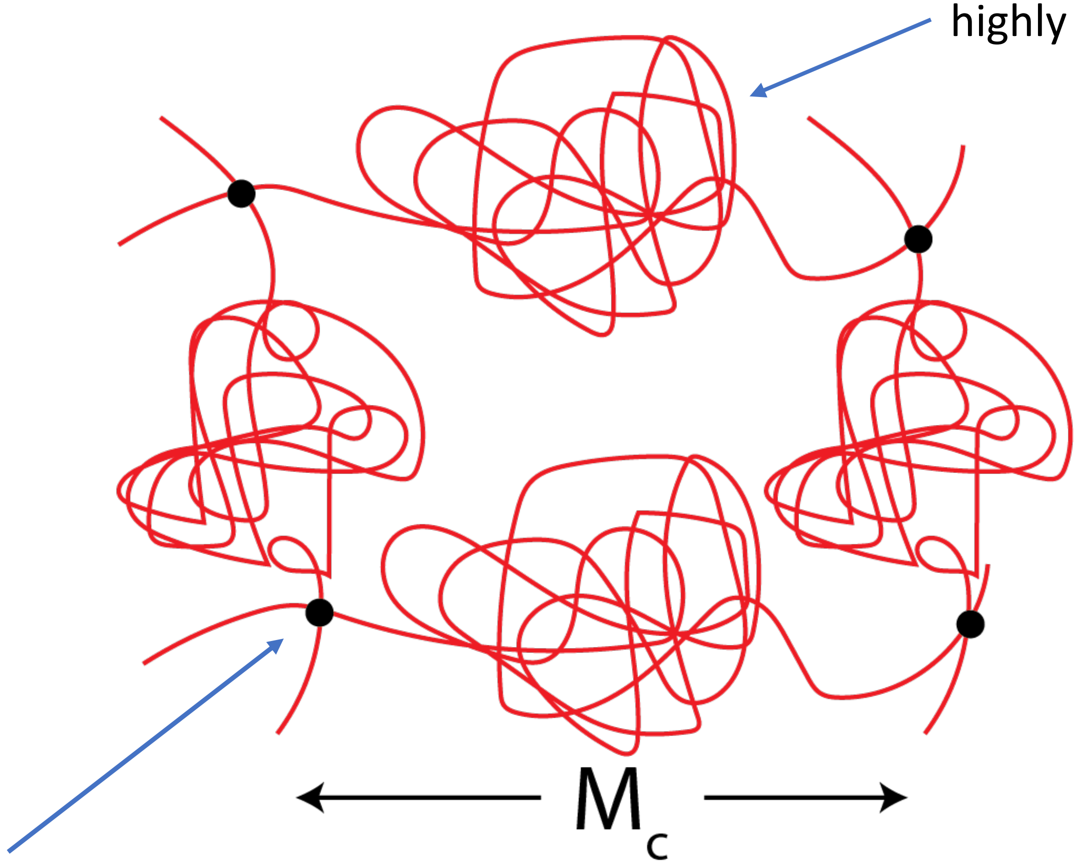
What is a rubber or "elastomer"?



$$\sigma = E\varepsilon$$

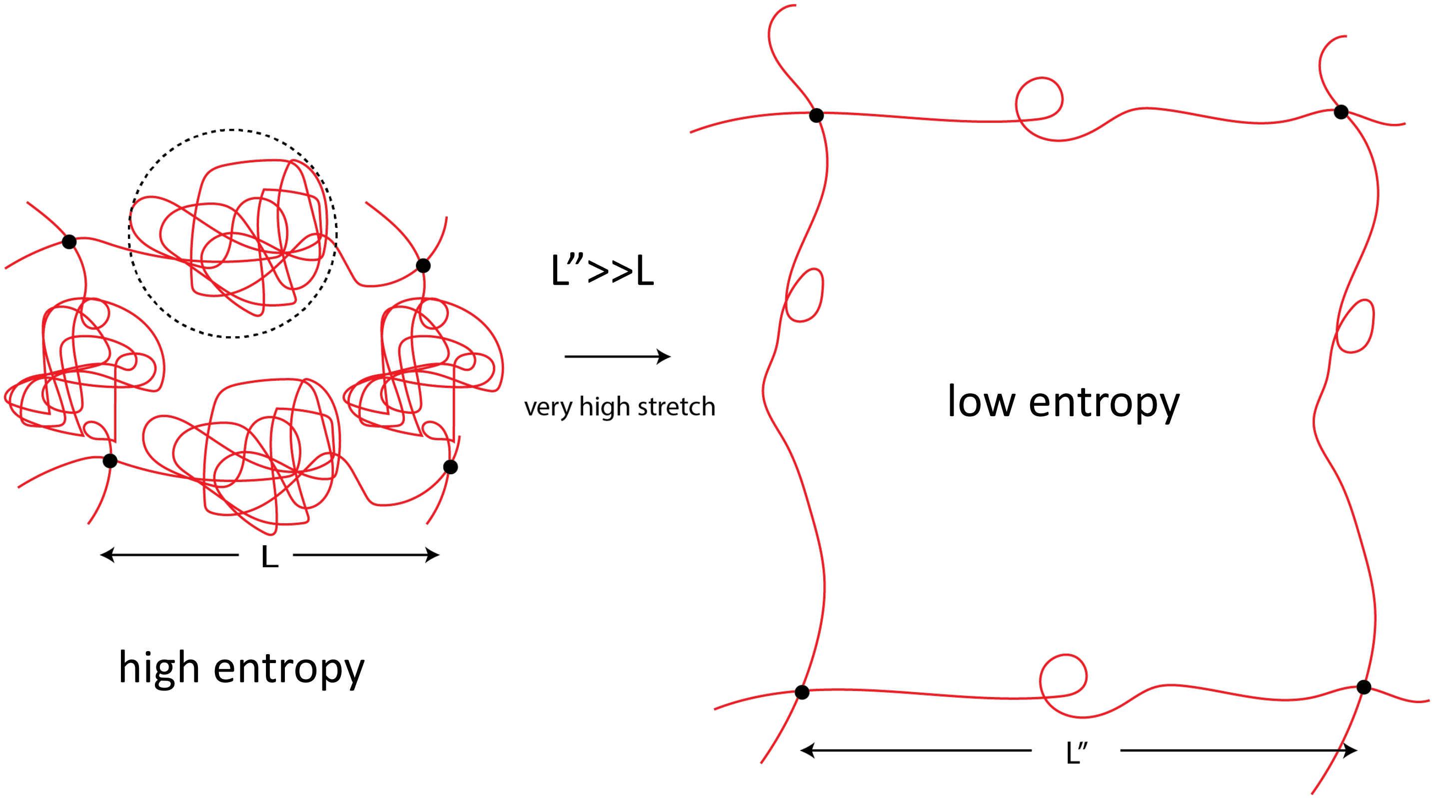
(holds for very low strains in rubber)

Molecularly, the rubber looks like this…



It is highly disordered or “entropic”; think of a bowl of spaghetti

If you “moderately” stretch it



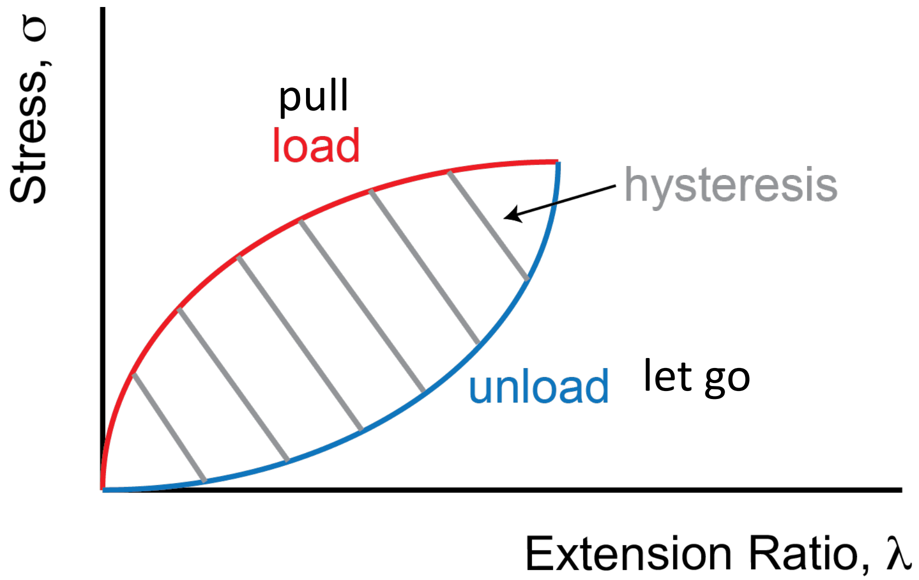
This is why a rubber band immediately snaps back after stretching and releasing it: it does not want to be in the lower entropy state but rather the high entropy state.

Rubbers are “soft” because their resistance to deformation is not from primary bond stretching but from coil deformation and uncoiling.

Rubbers store and return energy

Rubbers will store and return a portion of an imposed strain energy while the rest is lost as heat:

Strain energy in (pull rubber band) = Strain energy out (rubber band snaps back) + Heat

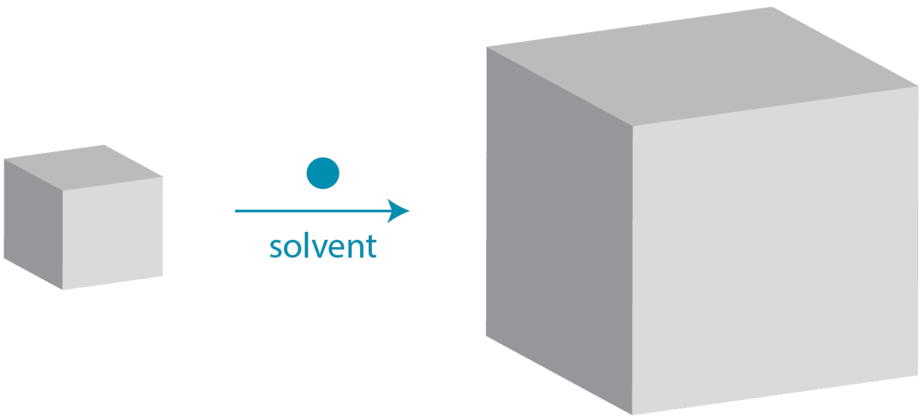


$$Hysteresis(\%) = \left(\frac{A_{load} - A_{unload}}{A_{load}}\right) * 100$$

$$Efficiency(\%)\ or\ \text{“}Resilience\text{”}, R = 100 - Hysteresis$$

Solvent swelling of rubber

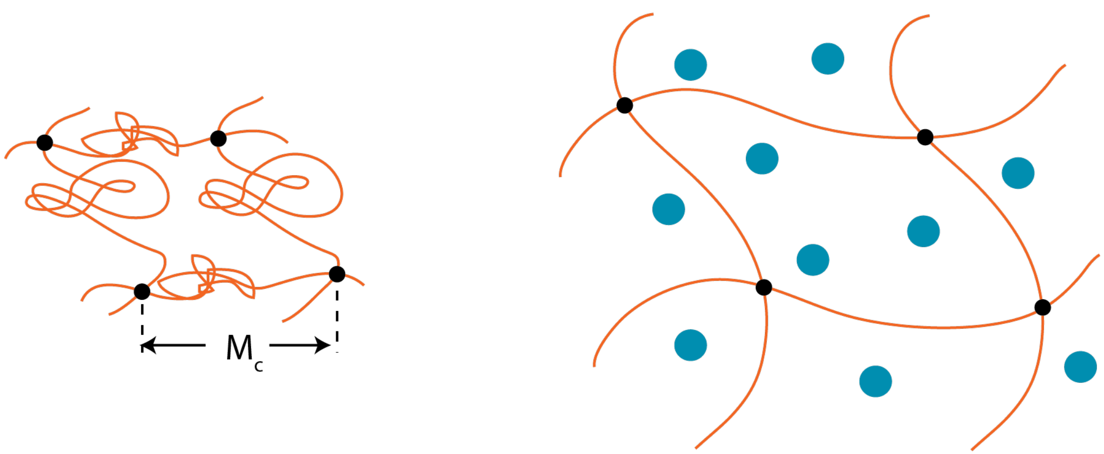
Besides hyperelasticity and entropy-dominated elasticity, rubbers can also be highly swollen with suitable solvents. Many rubber products contain small molecular weight liquids as additives to improve processing and performance. Biological structures (like you) can be considered a hydrogel or water swollen biological polymer/rubber.



volume swelling ratio

$$Q = \frac{V_T}{V_p} = \frac{1}{\nu_p}$$

ν_p=polymer volume fraction in solvent swollen rubber



Some biomechanics examples

We discussed the basic structure of elastomers and solvent swollen elastomers because natural biological elastomers are water (H_2O) filled proteins typically of high efficiency. They have structures that have evolved to do so.

“Catapult or Power Amplification Mechanism”
fleas, grasshoppers: https://www.youtube.com/watch?v=39EnHSg59mA

”Storing Energy for Flying”
locusts, fruit flies: https://www.youtube.com/watch?v=hduHsmk3QXM

“Storing Energy for Swimming”
Scallops: https://www.youtube.com/watch?v=NBH3UvlZo90
Jellyfish: https://www.youtube.com/watch?v=Q2zZ2S5esu8

“Return Springs”
Other bivalve mollusks that just use rubber to open close:
https://www.youtube.com/watch?v=6ceeZZ27GhY
R~96-97% for scallops, R~80% for others (the amino acid sequence has more glycine, G)

Many others: Human Achilles tendon to store energy for running, ungulates able to snap neck back up, elastin in arteries to help blood flow, flagelliform silk, etc.

Proteins are made of amino acids

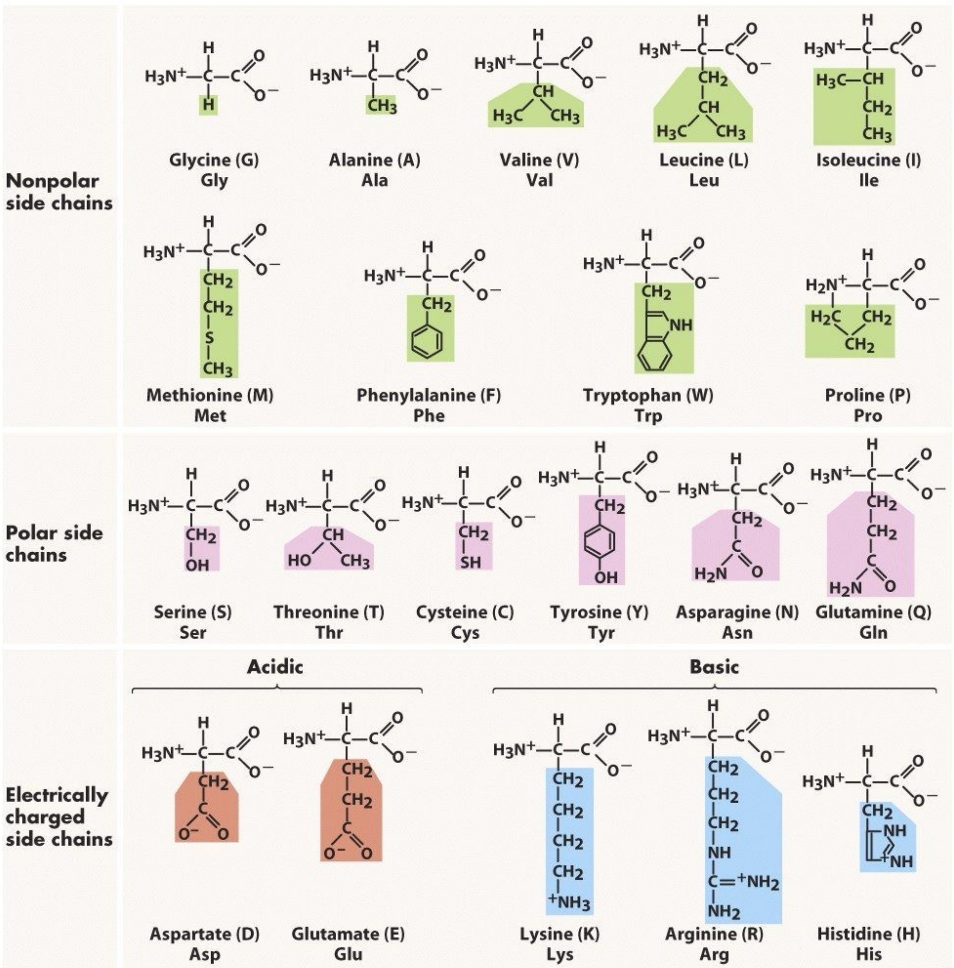
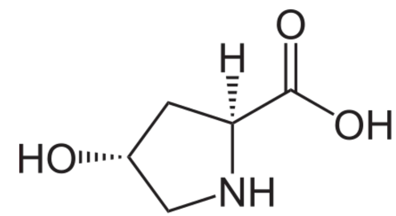


Figure 3-5 Biological Science, 2/e



Hydroxyproline (O)
Hyp

Proteins are polymers where the monomers are amino acids.

Protein elastomeric repeats

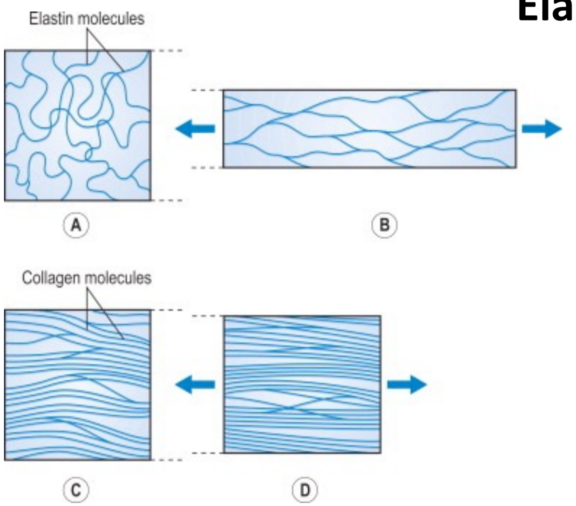
G-rich:
Abductin: FGGMGGGNAG, GGFGGMGGGX (disulfide bonds)

G-, P-rich:
Elastin: VGVAPG, VGVPG, VPGG, VGGLG, LGGLG (desmosines, isodesmosines, lysinonorleucines, (dehydro)lysinonorleucines)
Resilin: PGGGNGGRPSDTYGA (N-terminal repeat), PGGQDLGGYSGGR (C-terminal repeat) (tyrosines)
Flagelliform silk: GPGGSGPGGY (β-sheets)
Collagen: GXY (GPA, GPV, GKS, GAO) (GPO triple helix)

G-, P-, Q rich:
Glutenin: PGQGQQ, GYYPTSPQQ (disulfide bonds)
Dragline silk: GPGQQ, GPGGY, GGYGPGS (β-sheets)

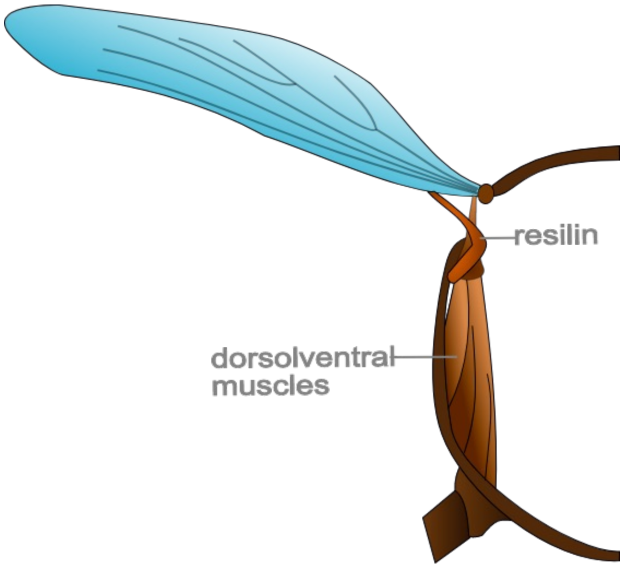
Biological elastomers exist in a complex environment

Elastin and Collagen

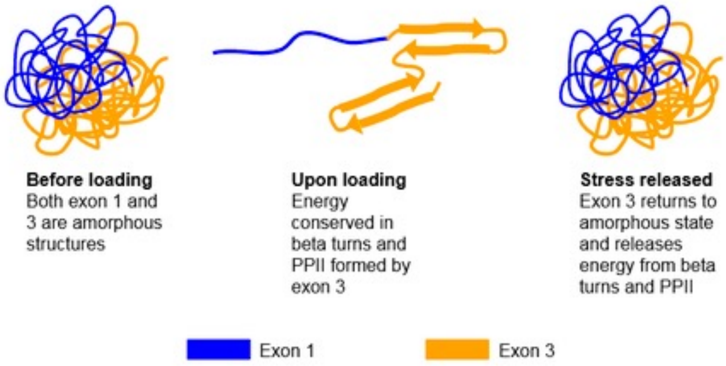


Elastin and collagen appear together. Both appear near fat and muscle.

Collagen appears with proteoglycans (sugars).



Resilin Resilin and chitin (sugar) appear together.



Resilin, R~96-97%
Most synthetic rubbers, R~60-80%

Biological elastomers in biomechanics

Biological elastomers that serve biomechanical functions in animals and insects are:

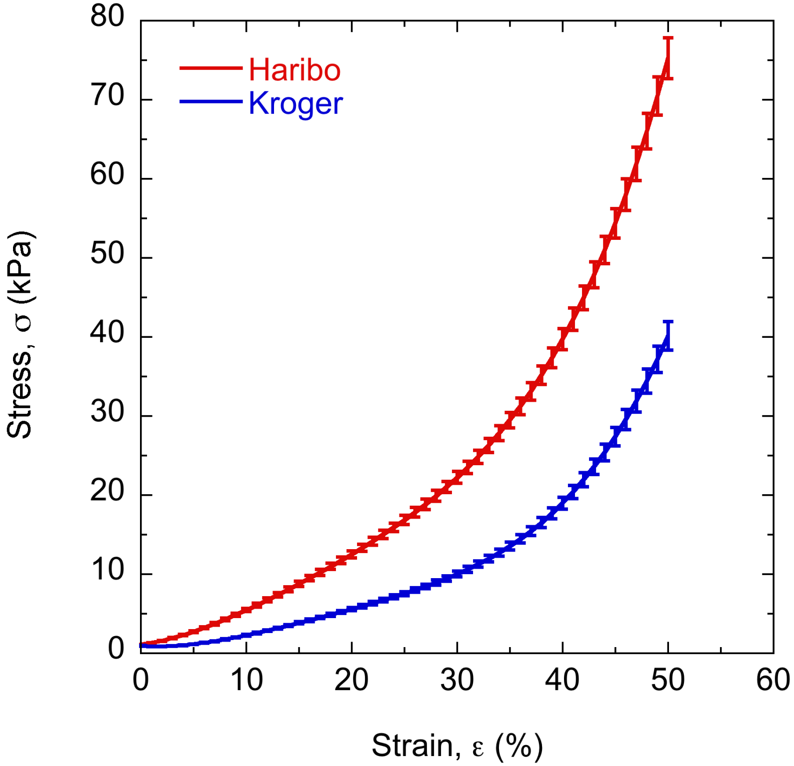
- a fringed micelle protein structure
- surrounded by water
- and sugars
- and possibly fats and other molecules

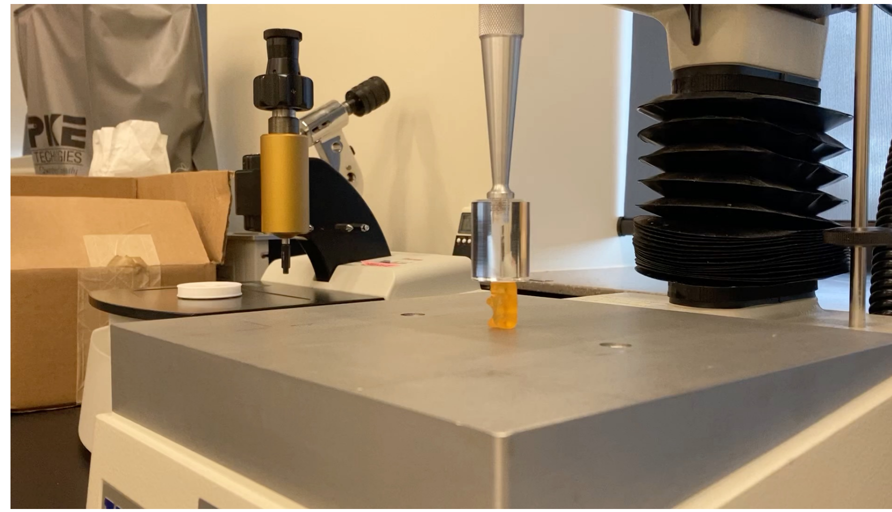
You know what this is?

A gummy bear!

Gummi ("rubber") bears

The Haribo gummy bears resist the squishing more!





Kroger gummy bears are 58% less stiff

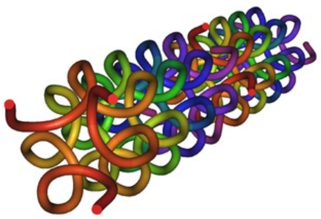
Haribo: GLUCOSE SYRUP (FROM WHEAT OR CORN), SUGAR, GELATIN, DEXTROSE (FROM WHEAT OR CORN), CONTAINS LESS THAN 2% OF: CITRIC ACID, ARTIFICIAL AND NATURAL FLAVORS, PALM OIL, PALM KERNEL OIL, CARNAUBA WAX, WHITE BEESWAX, YELLOW BEESWAX, YELLOW 5, RED 40, BLUE 1. MAY CONTAIN: WHEAT, TRACES OF MILK.

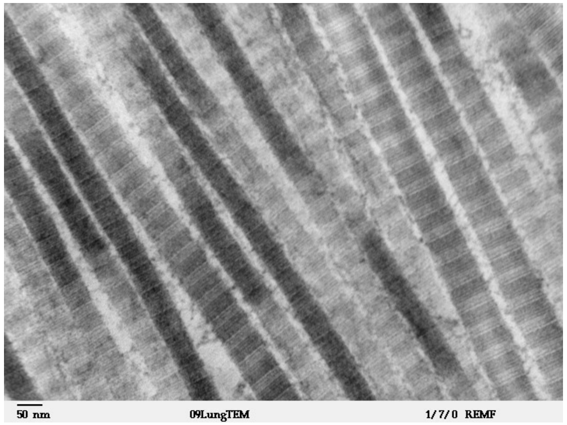
Kroger:

Corn Syrup, Sugar, White Grape Juice from Concentrate, Gelatin, Citric Acid, Sorbitol, Natural & Artificial Flavors, Carnauba Wax, Red 40, Yellow 5, Yellow 6, Blue 1

Gelatin is a biological elastomer

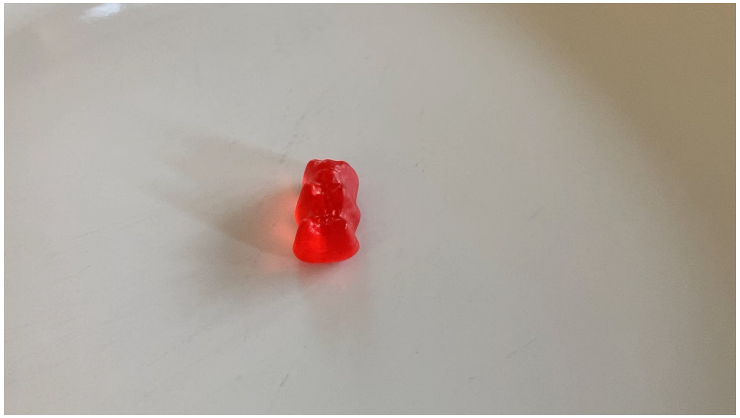
gelatin (nice fringed micelle)





collagen

lots of H_2O
a little sugar

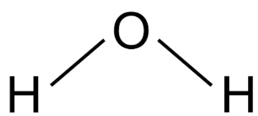


a little H_2O
lots of sugar

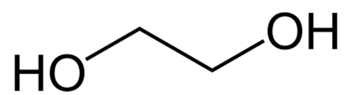
Mix small molecules and sugars w/ gelatin

1:2271 mol:mol gelatin:added liquid; syrups = 3:1 mol:mol H_2O:sugar
All formulas based off a commercial gummy candy formulation

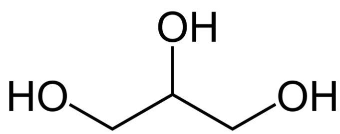
linear:



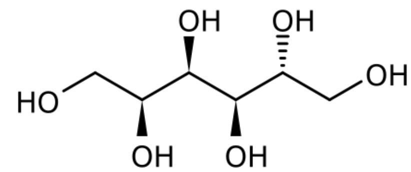
water



ethylene glycol

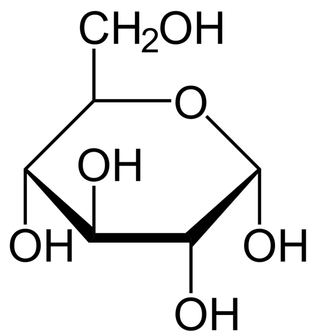


glycerol

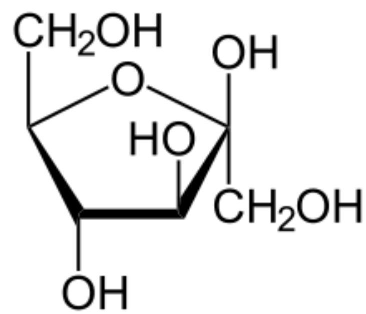


sorbitol

ring:



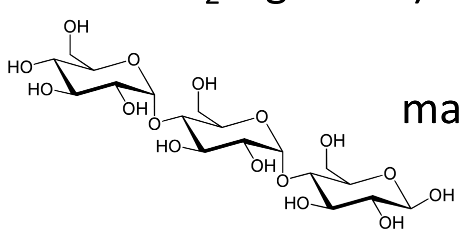
glucose



fructose

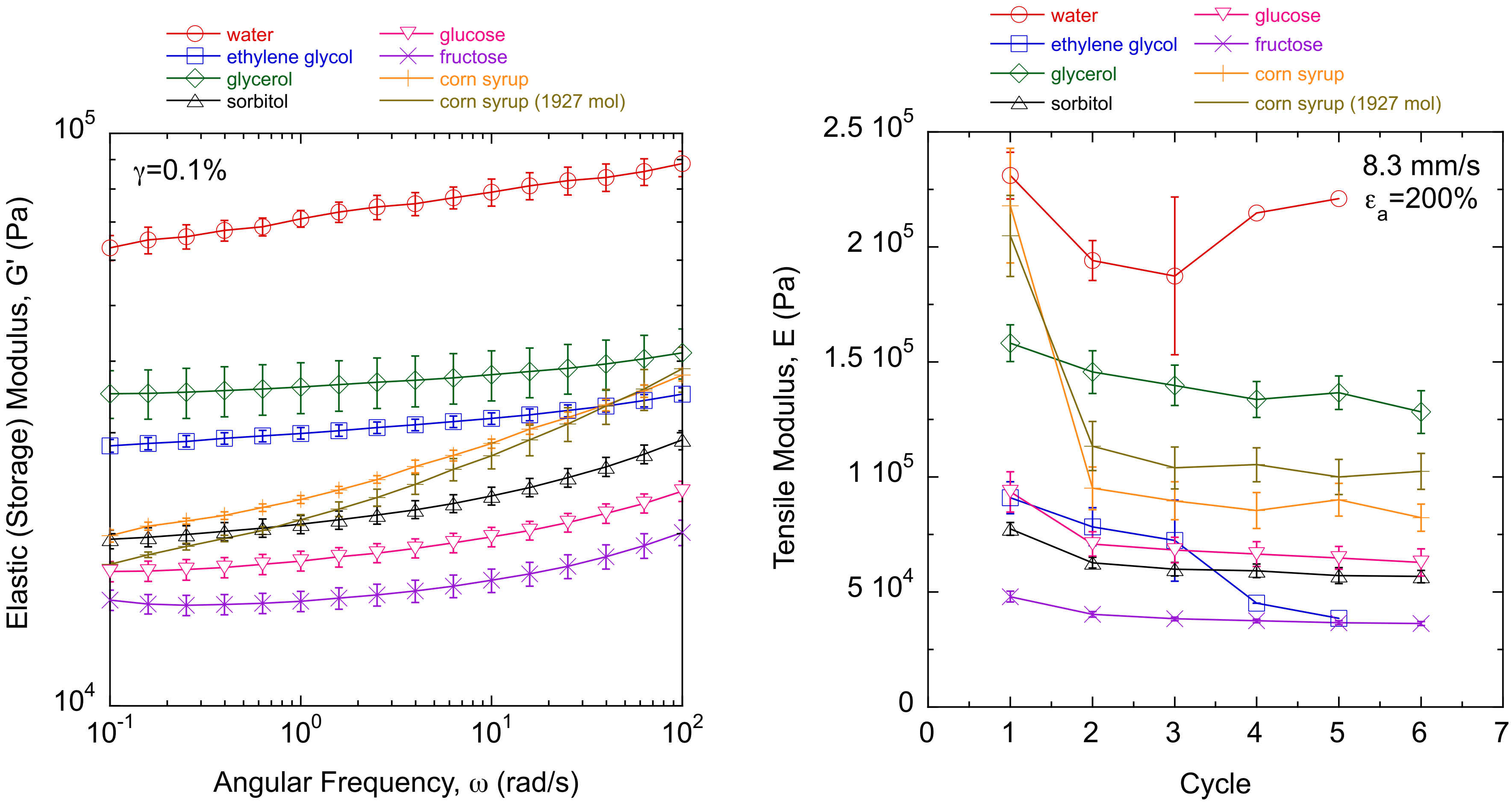
mixture:

corn syrup (lit values): ~19% glucose, ~11% maltotriose, ~56% higher mol. wt. sugars, ~14% H_2O (we measure 23%, gives 3:1 mol:mol H_2O:glucose)

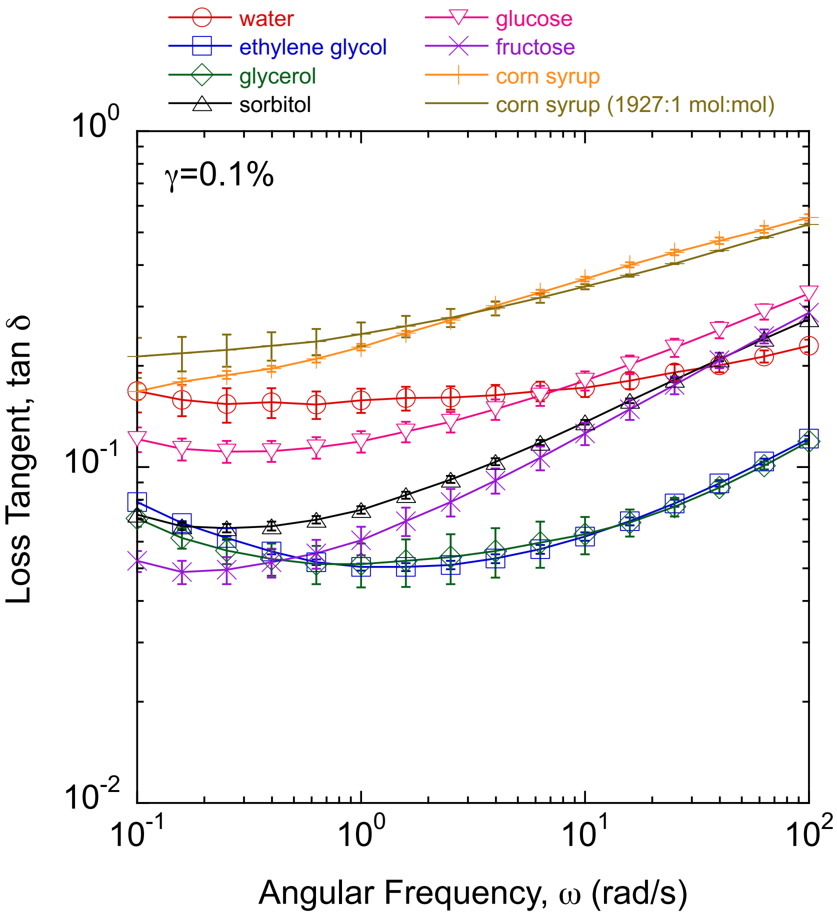


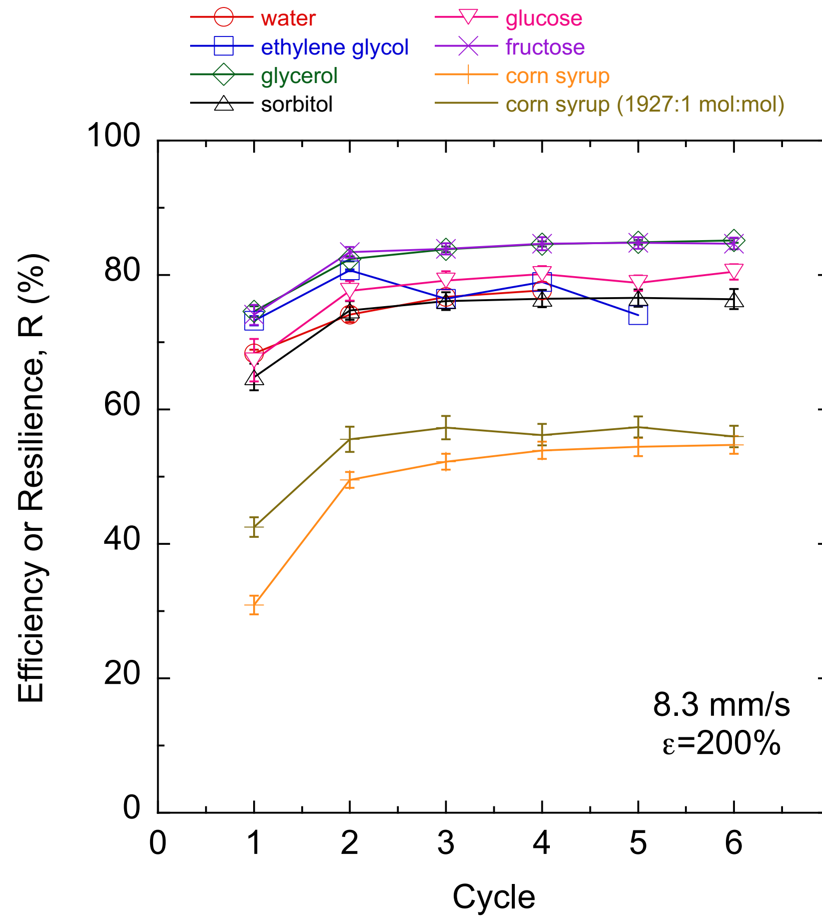
maltotriose (3 glucoses)

The sugar affects the network stiffness

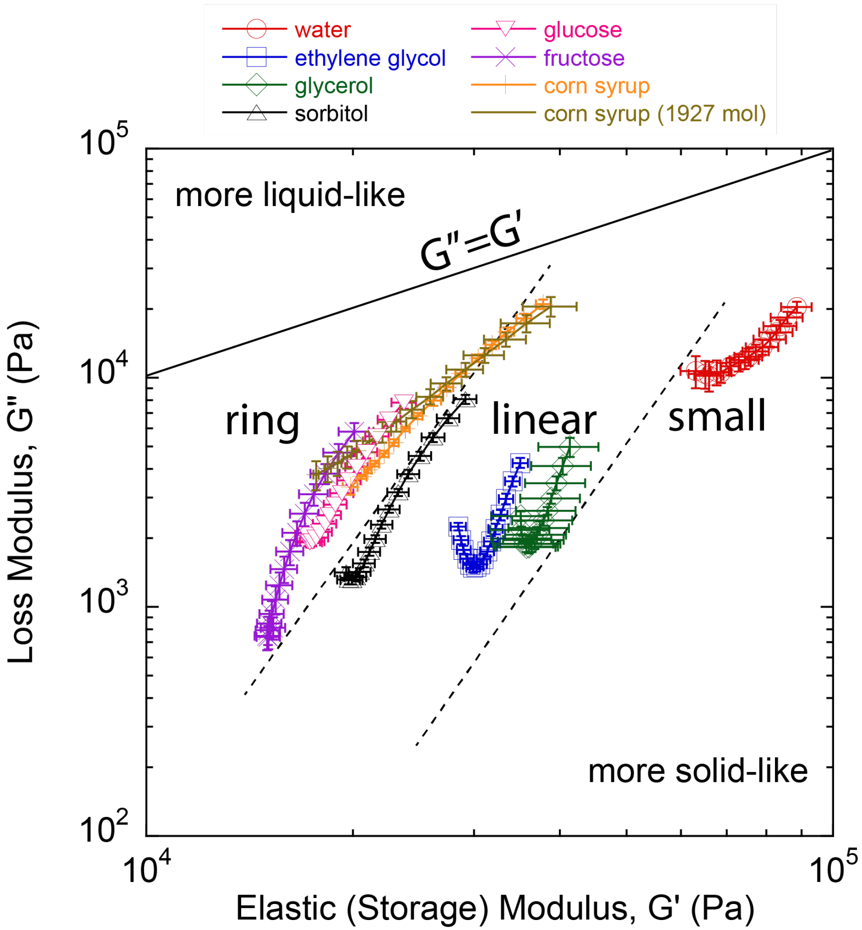


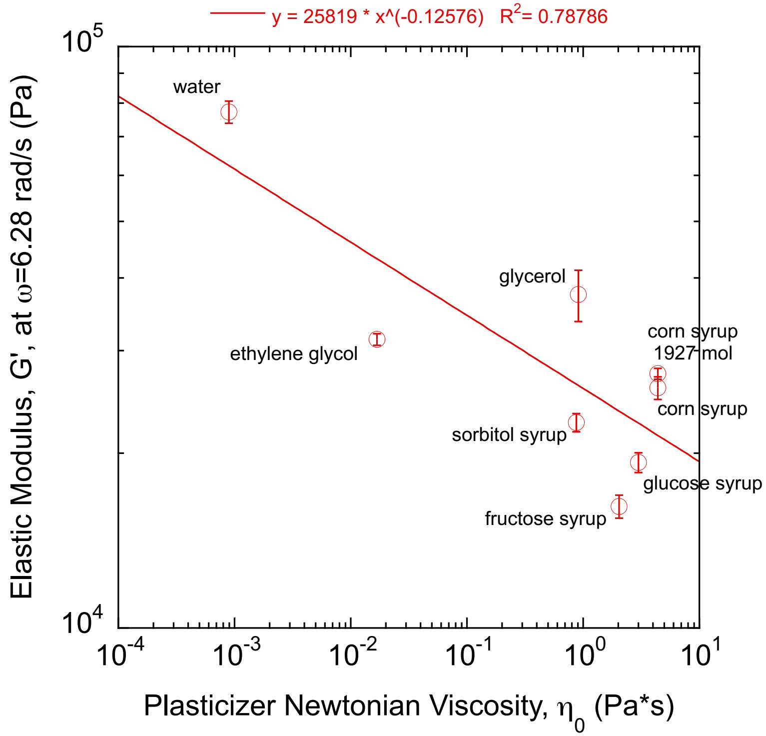
The sugar affects the rubber efficiency





The sugar affects the network structure





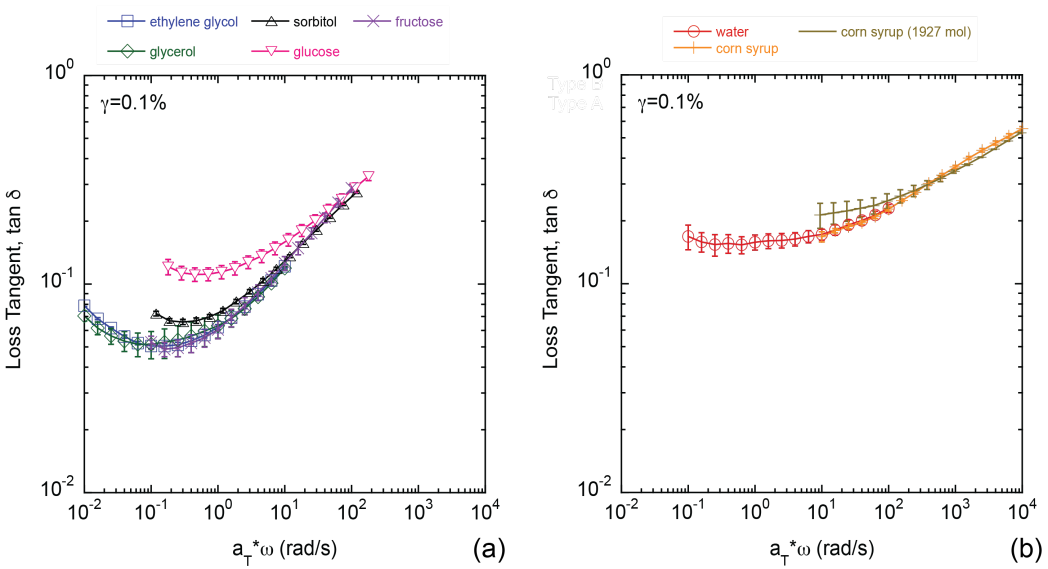
Added Liquid	M_c (g/mol)	
water	35,992	
ethylene glycol	89,418	*
glycerol	78,914	*
sorbitol	120,670	
glucose	142,033	
fructose	170,797	*
corn syrup	114,117	
corn syrup (1927:1 mol:mol)	120,046	

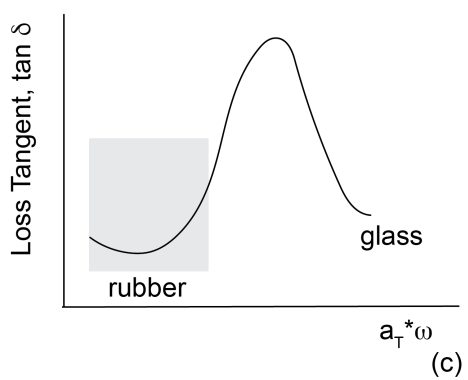
$$G' = \frac{\rho RT}{M_c}$$

*most efficient

What influences efficiency?

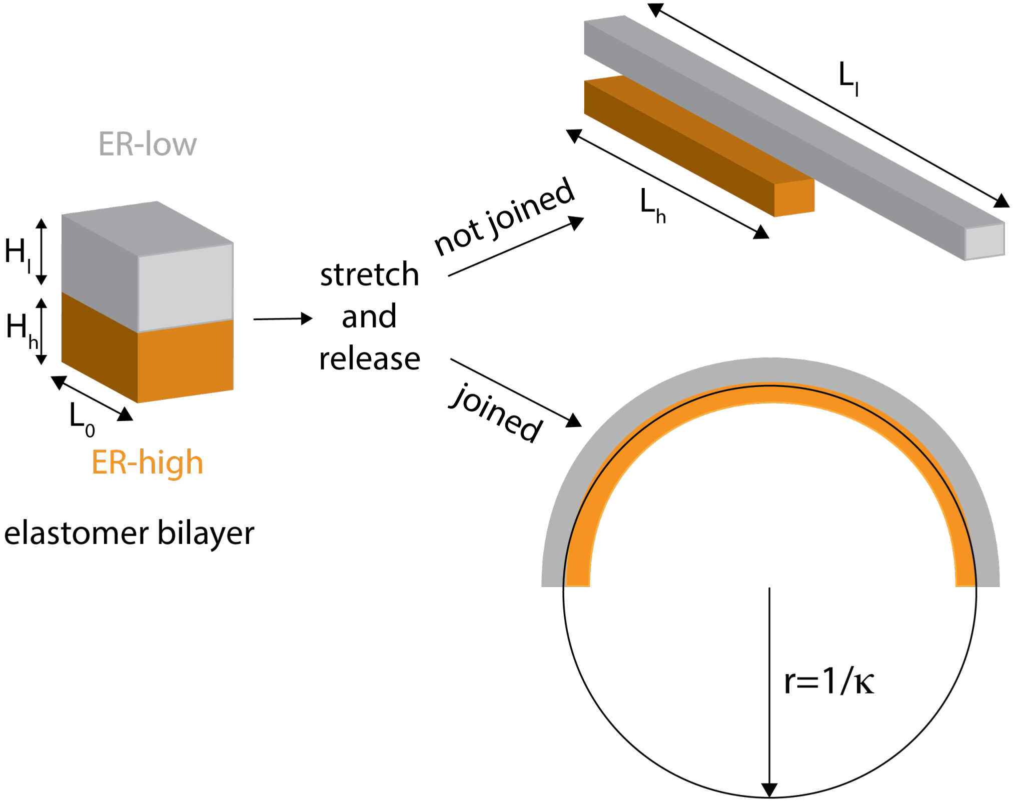
different shifting: different molecular mechanisms





- Being far from the glass transition, i.e., squarely in the rubbery region (see unshifted tan δ data).
- Having a lot of exposed CH_2 groups to maintain entropy in an aqueous environment (see sugar structures).

Creating bioelastomer devices



Viscoelasticity allows for the time dependence: use for gripping or motility with designed efficiency.