

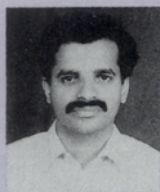
Why Does a Rubber Ball Bounce?

The Molecular Origins of Rubber Elasticity

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Rubbers are a fascinating class of materials because several of their unique properties have no parallel in the non-polymeric material world. In this article, the molecular origins for this unique behaviour will be addressed.

Rubber and rubber-like materials are fascinating because they exhibit a unique combination of two characteristics, (a) they can sustain very high elongation without rupture (5-10 times their original length is fairly common) and (b) spontaneous recovery to essentially their original state, with little or no permanent deformation. Natural rubber was one of the early materials to exhibit such properties, but these properties are by no means unique to this or any other specific class of polymers. In fact, there are now a wide range of materials that can exhibit such rubber-like characteristics. One common feature of all these materials is that they are all polymeric in nature. The structures of some of the commonly used rubbers are shown in *Table 1*.

In this article, we shall trace the molecular origins of rubber elasticity and delineate the essential criteria for materials to exhibit rubber-like characteristics.

Long Chains are Essential

All rubbers are polymeric in nature. Polymers, unlike small organic molecules, are very large (often 1000 to 10000 times the molecular weight of simple organic molecules, like ethanol or benzene) and by virtue of their size, these linear molecular chains are capable of adopting a wide range of conformations by rotation around the linking chemical bonds.

Rubber	Structure	T_g (°C)
Nitrile rubber	$\text{-(CH}_2\text{-CH(CN))}_x\text{-(CH}_2\text{-CH=CH-CH}_2\text{)}_y\text{-}$	-40
Styrene butadiene rubber	$\text{-(CH}_2\text{-CH(C}_6\text{H}_5\text{))}_x\text{-(CH}_2\text{-CH=CH-CH}_2\text{)}_y\text{-}$	-50
Chloroprene rubber	$\text{-(CH}_2\text{-CH=C(Cl)-CH}_2\text{)}_n\text{-}$	-50
EPDM	$\text{-(CH}_2\text{-CH}_2\text{)}_x\text{-(CH}_2\text{-CH(CH}_3\text{))}_y\text{-}$	-55
Natural rubber	$\text{-(CH}_2\text{-CH=CH-CH}_2\text{)}_n\text{-}$	-73
Butyl rubber	$\text{-(CH}_2\text{-C(CH}_3\text{)}_2\text{)}_x\text{-(CH}_2\text{-C(CH}_3\text{)=CH-CH}_2\text{)}_y\text{-}$	-73
Cis-butadiene rubber	$\text{-(CH}_2\text{-CH=CH-CH}_2\text{)}_n\text{-}$	-100
Silicone rubber	$\text{-(O-Si(CH}_3\text{)}_2\text{)}_n\text{-}$	-127

Table 1 Effect of chemical structure on T_g of various rubbers.

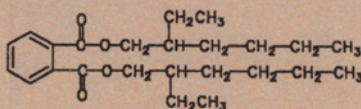
Flexibility of the Polymer Chains

The presence of long polymer chains is essential, but certainly not sufficient for the material to exhibit rubber elasticity. A further important criterion is that the polymer chain segments should have sufficient conformational mobility at the desired temperature of use, typically at ambient temperatures. This suggests, firstly, that the sample should contain a fairly significant fraction of amorphous regions, and more importantly, its glass transition temperature (T_g) should be significantly lower than the ambient temperature, typically 50-60 degrees lower (note that most of the polymers listed in *table 1* meet these criteria). Glass transition temperature is characteristic of amorphous polymers (or amorphous regions of a semicrystalline polymer) and may be defined as the temperature at which the onset of

Glass transition temperature may be defined as the temperature at which the onset of segmental motion occurs.

Box 1

Plasticizers are medium sized organic molecules, typically esters of carboxylic acids or phosphoric acids, that are used to make polymers plastic i.e., soft and pliable; in other words lower the glass transition temperature. One of the most commonly used plasticizer is dioctyl phthalate (DOT), which is actually the 2-ethylhexyl diester of phthalic acid.



DOT

A majority of the plasticizers manufactured (>70%) is used in polyvinyl chloride (PVC) formulations, to bring down its processing temperature and also to transform PVC from its hard, brittle state (as in PVC pipes used in plumbing) to a soft and flexible form as in vinyl sheets (used in vinyl table covers).

segmental motion occurs, i.e., long segments of the polymer backbone acquire adequate mobility to rearrange on application of any kind of stress. Macroscopically, an amorphous polymeric material becomes soft and rubbery above T_g , while it is hard and often brittle below it. So, in principle, all polymers are capable of exhibiting rubbery behaviour, provided the temperature is appropriately selected. Alternatively, a plasticizer can be used to bring down its T_g to the desired temperature (see *Box 1*).

An additional structural feature that is important is the inherent conformational flexibility, i.e., the fraction of the total backbone chemical bonds that possess rotational freedom, implying that the barriers to rotation should be surmountable at a reasonable temperature prior to its chemical degradation. This, of course, is easily achieved in polymer molecules that are largely made up of C-C, C-O or Si-O single bonds. Bulky substituents on the polymer backbone are generally detrimental, as they would increase the barriers to rotation.

Crosslinkability

In addition to the two characteristics mentioned above, a further important requirement is the ability of the polymeric system to

Crosslinking is the process by which the individual polymer molecules (or chains) are linked together by chemical bonds or strong non-covalent interactions.

undergo *crosslinking*. Crosslinking is the process by which the individual polymer molecules (or chains) are linked together by chemical bonds or strong non-covalent interactions like, hydrogen-bonds. The presence of unsaturation in natural rubber, *cis*-poly(1,4-isoprene), provides the necessary reactive functionality for further reaction to generate chemical crosslinks. A process that is most often used in natural rubber that creates such crosslinks, is called *vulcanization*.¹

¹ The chemistry of vulcanization is explained in the accompanying article.

This kind of crosslinking is essential to impart the second of the two characteristics of rubber, namely, spontaneous retraction. In an un-crosslinked system, when a stress is applied the chains will indeed straighten out (as shown in *Figure 1*), but at higher elongation they will slip past each other and would result in an irreversible deformation of the sample.

In a crosslinked system, on the other hand, this slippage is arrested by the presence of crosslinks that hold all the polymer chains in the sample together. Thus, when the stress is removed, the sample would retract to its original state. While crosslinking is essential, it is also critical that the right amount of it be present to impart ideal rubber characteristics. In other words, the polymer segments in between the crosslink junctions should be sufficiently long to permit chain reorganization on application of stress. Typically, crosslinking conditions employed for rubber ensure that, on an average, one out of every 50 -100 repeat (monomer) units, say in natural rubber, is involved in forming the inter-chain crosslinks. At higher crosslink densities, the extension of

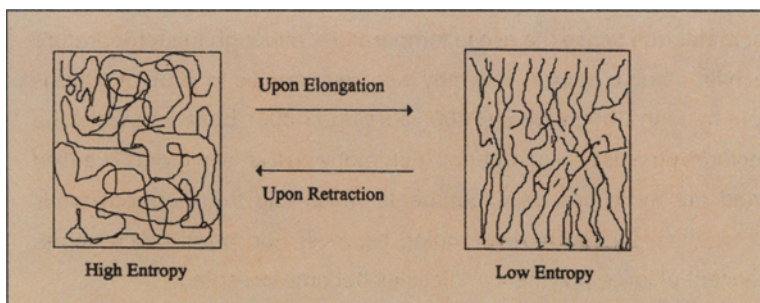


Figure 1

Thermoplastic elastomers possess elastomeric properties at ambient temperatures, but can be made to flow at higher temperatures.

the rubber would be greatly reduced and eventually at very high crosslink densities it would no longer possess any elongation. At this point it will essentially behave like any other thermoset resins, such as Bakelite. Unlike natural rubber based elastomers, which once crosslinked do not retain their liquid-like flow property, there exists a class of so-called segmented block copolymer (commonly based on polyurethanes) which possess elastomeric properties at ambient temperatures, but at the same time can be made to flow at higher temperatures (implying that they are melt processable). This class of materials are called *thermoplastic elastomers*, of which the most popular is the one based on polyurethanes and goes by the trade name *Spandex*. In such elastomers, there are no chemical crosslinks, but only those based on strong hydrogen-bonds (between the urethane -NH-CO-O- segments) that do not give way at ambient temperatures but are easily broken at higher temperatures.

The Underlying Thermodynamic Principles

Early experiments had shown that when elongation of rubber is done rapidly (almost adiabatically), it causes the temperature of the rubber to rise, suggesting exothermicity (see *Box 2*).

In general, the change in internal energy dE accompanying the stretching of an elastic body can be equated to the work done

Box 2

Hold a rubber band in contact with your lips and stretch it in one swift and rapid motion. Your lips will serve as a highly sensitive thermometer and sense the rise in temperature, although the temperature rise is rather small and often much less than a degree. You may also be surprised to learn that this is one of the experiments carried out by John Gough, almost 200 years ago (1806), based on which he postulated some of the first conjectures on elasticity of rubber. Later, many well known giants like Lord Kelvin, Clausius and Joule carried out more precise experiments which laid the thermodynamic foundations for rubber elasticity. The molecular level understanding, however, had to wait much longer, almost till the 1930's when the concept of large polymeric molecules became accepted.

dW and the heat absorbed or expelled by the body, in the following fashion.

$$dE = dQ - dW$$

The exothermicity (dQ) can hence arise from either or both of the terms dW and dE . More accurate experiments done later have unequivocally shown that there is essentially no change in the internal energy of the rubber (up to a certain elongation of about 300%) and that the exothermicity is essentially equal to the work done on the system in elongating it. Under these circumstances, the retraction of rubber may be stated to have its origin only in the entropy change. This is indeed the case as stretching of rubber causes a greater ordering of the polymer chains (see *Figure 1*) and hence its entropy decreases (i.e., ΔS is negative). At a molecular level, stretched polymer chains can sample a much smaller number of possible chain conformations, and hence have a lower conformational entropy. Thus, the elasticity of rubber can be solely attributed to the unfavorable change in its entropy and hence it exhibits an *entropically derived elasticity*. At much higher extensions, the polymer chains actually arrange themselves close enough to cause crystallization, and under these circumstances the internal energy (E) actually decreases, causing a further rapid increase in exothermicity. At room temperature, on releasing the applied stress, the crystallites melt and the original state is recovered.

The elasticity of rubber can be solely attributed to the unfavourable change in its entropy and hence it may possess an entropically derived elasticity.

Bounce of a Rubber Ball?

Consider dropping a rubber ball on a hard surface. When it hits the ground, the stress due to the impact causes the molecules of rubber to deform or reorganize. Thus, work is done on the system. This work is either completely or partially transformed into potential energy of strain, and the ball is in a state of strain. When the external forces are withdrawn the molecules will retract partially or completely to its original state. Then the stored potential energy is recovered in the form of external work, i.e., bouncing.





Figure 2

For a perfectly elastic body, the work done by the external forces during deformation is completely transformed into potential energy of strain. But in the case of a partially elastic body, a portion of the work done is transformed into heat. Hence, a perfectly elastic body (which is, of course, non-existent!) recovers its original shape after unloading, but a partially elastic one does not. This is illustrated in *Figure 2*. Here, the Young's storage modulus E' is a measure of the energy elastically stored (by molecular deformation). The ball obviously does not reach the initial height because of the dissipated energy (usually, dissipated as heat) E'' .

So the next time you bounce a ball, use a rubber gasket, or ride a bicycle, think of the many polymer molecules that are constantly reorganizing to suit your convenience!

Acknowledgement

VGG expresses deep sense of gratitude to Baby Kuriakose, Rubber Research Institute of India, Kerala, for creating immense interest in rubber technology.

Suggested Reading

- ◆ P J Flory. *Principles of Polymer Chemistry*. Cornell University Press. Ithaca. N.Y., 1953.
- ◆ L H Sperling. *Introduction to Physical Polymer Science*. 2nd Edition. John Wiley and Sons. Singapore, 1993.

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Fermi's aversion to mathematical technicalities is well known. Even when a mathematical argument had played a role in his initial thinking of a problem, he was careful to erase all its traces from his final account. I was once to talk to a seminar and when I expressed my doubts as to what I should talk about, he advised, "If I were you, I would not be technical." And I asked, "Do you mean, if I were you or you were me?" This baffled him: it was the only occasion I got the better of him.

S Chandrasekhar