RUBBER THERMODYNAMICS

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The erratic behavior of rubber on hot days and the decay of torque in a wound motor when a model is held for some time before launching are facts of life recognized by rubber flyers without any fancy measurements. Although the following discussion yields no complete solution to these problems, a little insight may help you be more philosophical the next time you blow a fuselage.

Physical chemistry textbooks often treat rubber by analogy with an ideal gas — stretching the rubber being equivalent to compressing the gas. In both cases, "ideal" behavior breaks down at some point in the process when molecules begin to interact. In a gas, at sufficiently high pressures, this interaction will result in a change of phase to the liquid state. In rubber, there is a somewhat comparable transformation to an ordered, crystalline structure. Using the gas analogy, the tension in a rubber band is given by[1]:

$$\text{Tension (K)} = -T(\partial S / \partial l)_T + (\partial E / \partial l)_T \tag{1}$$

Where:

T = temperature

S = entropy, a quantity used in thermodynamics as a measure of the disorder in a system. Stretching a rubber band decreases the disorder, hence the negative sign for this term.

l = length of rubber

E = internal energy of the rubber

It turns out experimentally that the tension is directly proportional to temperature (again, up to that certain point) so that the second term in the right side of the above equation may be neglected, just as for an ideal gas, leaving:

$$K = -T(\partial S / \partial l)_T \tag{2}$$

Kuhn and Grun[2] have shown that for a rubber band stretched from a length l_o to a new length 1, the change in entropy is given by:

$$S - S_o = (-1/2 Nk)(\alpha^2 - 2/\alpha - 3) \tag{3}$$

Where:

N = concentration of molecules per unit volume

k = Boltzmann's constant

$$\alpha = \frac{1}{l_o}$$

from this,

$$(\partial S / \partial l)_T = (Nk/l_o)(\alpha - 1/\alpha^2) \tag{4}$$

substituting into equation (1)

$$K = (NkT/l_o)(\alpha - 1/\alpha^2) \tag{5}$$

so that the tension in a rubber band is directly proportional to the temperature and the concentration of polymer molecules in the rubber. The dependence on length is illustrated in Figure 1, plotted for l_o = resting length (no tension).

This brief look at the behavior of rubber in it's "ideal" region does give some useful information:

(1) The shape of the tension vs. length plot is good qualitative agreement with data obtained by George Xenakis — that is, after the rubber has been stretched to about 1.5 times its resting length, the tension increases almost linearly with length (until the rubber begins to behave non-ideally: dashed line). As I recall, on George's graphs this occurred around α = 5. There is then a long enough portion of the graph to get a good estimate of the slope of the almost-linear portion. This slope, $\frac{\partial K}{\partial \alpha}$

approaches $\frac{NkT}{l_o}$ as $\alpha \rightarrow \infty$ The quantity NkT is the modulus of rigidity in Hooke's law applied to an ideal piece of rubber; so I suspect that you can get a pretty good idea about the quality of a rubber motor by carefully measuring $\partial K/\partial \alpha$ in the linear region — without fatiguing it by winding to capacity.

(2) The direct relationship between tension and temperature has been known since 1805. This so-called "Joule effect" has been used in several devices which convert heat into mechanical energy via rubber bands (the Scientific American published several of these little

motors a while ago). The practical points are:

a) The tension in a rubber band stretched between two points will increase if the rubber is heated. If the ends of the rubber are not fixed, it will shorten. On a hot day, you just won't be able to get in as many turns — you have an effectively shorter motor. It is difficult to protect motors during winding from heat gain due to convection and conduction but it is probably helpful to shield from the sun. Pirelli being so dark, heat gain from radiation is probably significant.

b) As you stretch and wind a motor, its temperature rises — over and above the temperature changes due to environment and friction between strands. As it unwinds, it cools. Since this temperature rise is reflected in increased tension, or torque in a wound motor, it is desirable to prevent heat loss after the motor is wound. Jon Davis published some data on the decay of torque with time when a wound motor is held prior to launching (NFFS Symposium 1971). Some of this decay is undoubtedly due to heat loss. It may be helpful to cover the inside of the motor compartment with a highly reflective surface (I have used chrome mylar tape) and the outside with a dark, non-reflective surface (black tissue). I'm currently trying to get some experimental verification of this.

Most of the time, unfortunately, rubber flyers are dealing with motors wound to capacity — well out of the range of ideal behavior. As mentioned earlier, the deviation from ideality corresponds to a phase change in the rubber. X-ray diffraction studies have shown signs of crystallization in rubber with elongation as low as 80%. Vulcanization (the cross-linking of short isoprene chains by sulfide bonds) reduces the tendency to crystallize. One study of fully vulcanized rubber showed no X-ray diffraction evidence of crystallization at 400% elongation. It would be interesting to know what sort of vulcanization process is used in the manufacture of Pirelli.

To my knowledge, there is no satisfactory mathematical treatment for rubber which is crystallizing. Experimentally, it has been possible to get some idea of what goes on. Figure 2 is a plot of data obtained from reference 3. The plot of $\partial E / \partial 1$ vs. α shows that this derivative, which we neglected above, actually does have a small, fairly constant value up to some critical α. This represents the relatively insignificant change in the internal energy of "ideal" rubber on stretching. Beyond the critical point $\left(\frac{\partial E}{\partial 1}\right)_T$ rapidly acquires a large negative value. Physically, this represents loss of heat during crystallization. This large negative $\frac{\partial E}{\delta \ell}$ would tend to decrease tension, yet the tension continues to increase. It turns out that the $\left(\frac{\partial S}{\delta \ell}\right)_T$ in the Joule effect term rapidly acquires a larger value, more than making up for the loss in the $\left(\frac{\partial E}{\delta \ell}\right)_T$ term if the temperature stays constant. This again points up the importance (theoretically, at least) of preventing heat loss in a fully wound motor.

Another aspect of the crystallization phenomenon, reported by several authors, is a time lag observed between stretching and the appearance of a crystalline

X-ray diffraction pattern. The magnitude of this lag is said to range from seconds to hours depending on conditions. At any rate, it seems that winding slowly may be desirable to give the rubber time to "catch up." If you are using a winding tube, it's a good idea to wait at least a minute or so before pulling it out after winding. If the crystallization process has been lagging, the motor may blow while you're waiting to launch. On the basis of some empirical observations at Caddo Mills, Frank Parmenter has come to the same conclusion about leaving winding tubes in for a while.

References

1. Moore's Physical Chemistry, 3rd ed., Prentice-Hall Inc., Englewood Cliffs, New Jersey, pg. 776 (1962).

2. Kuhn, W. and Grun, F., Journal of Polymer Science, I, pg. 83, (1964).

3. The Chemistry and Technology of Rubber, an American Chemical Society monograph published by Reinhold Publishing Corp., New York, in 1937. The data plotted in Figure 2 are those on pg. 3373 of the monograph.
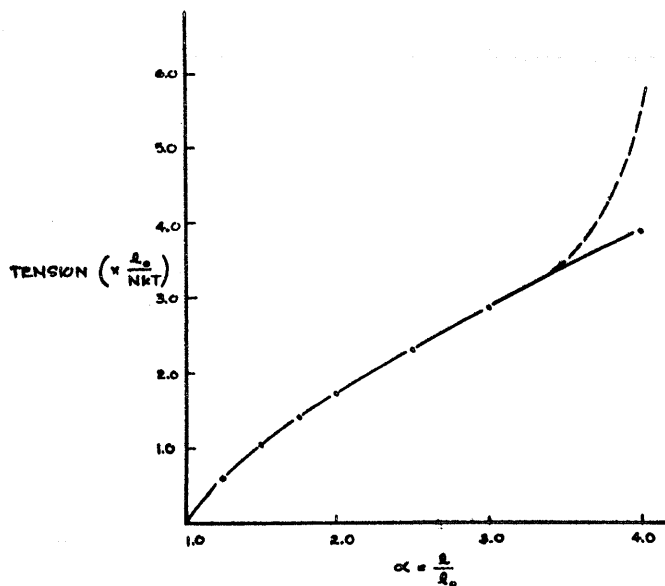
Figure 1

Plot of tension as a function of rubber length. The solid line is plotted from Equation 5, representing ideal behavior. The dashed line is sketched in to represent real behavior. An increase in temperature will increase the slope of line.
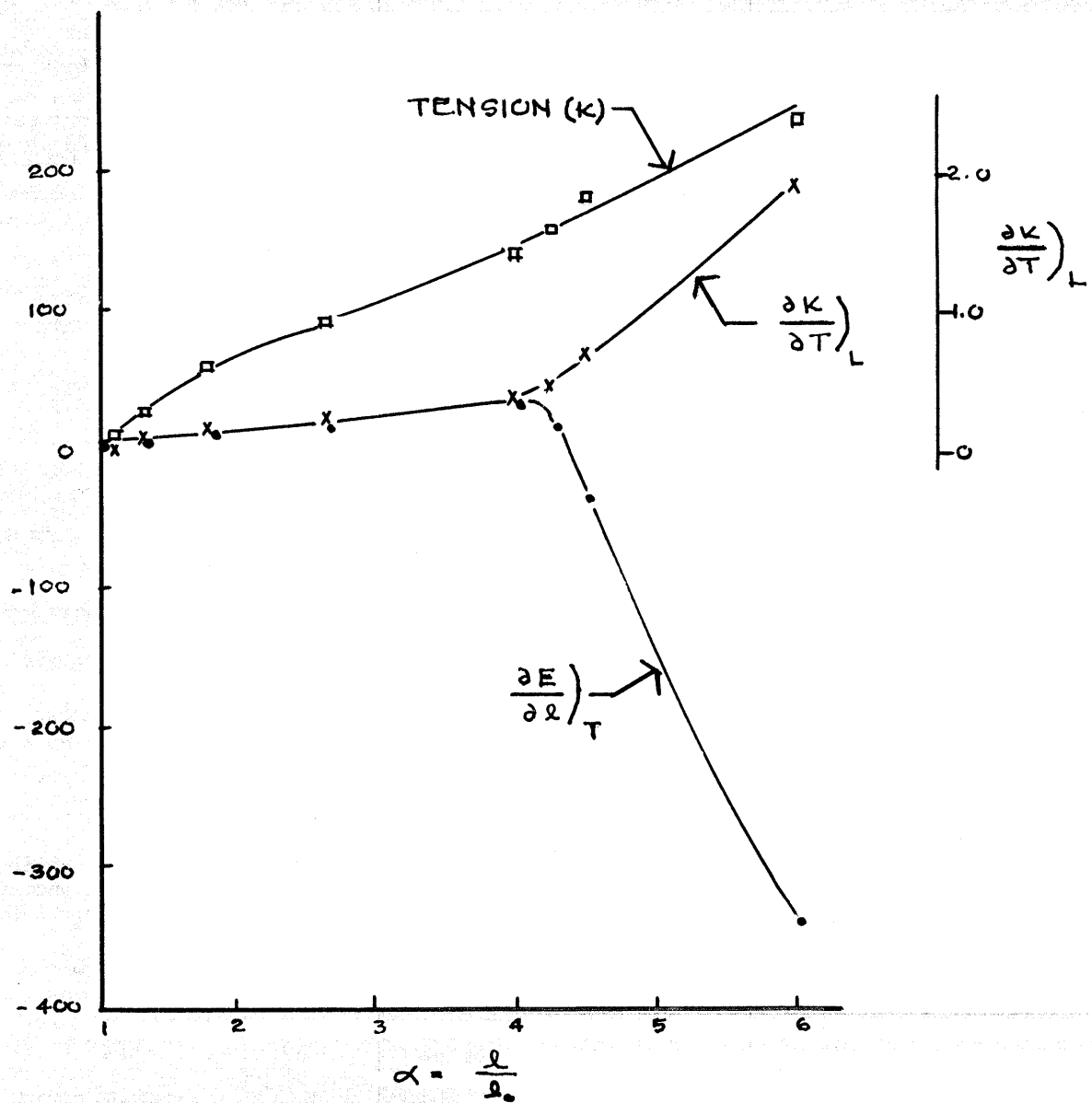
Figure 2

Data from Reference 3, plotted to show continuing increase in tension despite drastic changes in $\left(\frac{\partial E}{\partial \ell}\right)_T$ as crystallization sets in. This is explained by rapid non-linear change in the Joule effect term $\left(\frac{\partial K}{\partial T}\right)_L$