A relation between flexibility and thermal conductivity of polymers

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Abstract

Flexibility of polymers defined by an equation in 2019 is related here to thermal conductivity, using reliable data for both properties found in the literature. The resulting equation is simple, it has the form of a quadratic polynomial. The goodness of the fit represented by $R^2 = 0.975$, while $R^2 = 1$ represents a perfect fit. Thus, knowledge of one of these properties can be used for calculation of the other one. The present results are a part of a larger program enabling obtaining by calculation pertinent properties of polymers from other properties for which data are available.

Keywords: polymer flexibility; polymer thermal conductivity; polymer mechanics; polymer thermodynamics

1. Introduction

Flexibility of polymers is a property important in various applications. To give just one example, Lu, Lin, Liu and coworkers [1] have developed flexible high efficiency polymer solar cells on the basis of polyethylene terephthalate (PET) with imprinted Ag grid as transparent electrode. In 2019 flexibility Y of polymers has been defined by an equation [2]:

$$Y = V_{sp}/(\Sigma_i^n U_{bi}) \qquad (1)$$

Here V_{sp} is the specific volume of a given polymer in cm^3/g at a specified temperature while $\sum_i^n U_{bi}$ is the sum of the strengths of bonds in the monomer. The idea of working with the bond strength comes from the classical work of Linus Pauling [3].

The other polymer property we are interested in is thermal conductivity λ. As discussed by Sui and coworkers [4], thermal conductivity of polymers can be modified for instance by inclusion of carbon nanotubes (CNTs) – affecting for that matter electrical conductivity as well. Consider an element of a structure made from a polymer – such that a part of that element is in the sun and a part in the shadow. In an admittedly extreme example, a solar furnace at the Plataforma Solar de Almeria in Spain can reach a peak of solar energy absorption of 300 W/cm^2 [5]. We infer that in a variety of situations thermal conductivity of polymers is important.

As discussed in some detail in a textbook of Materials Science and Engineering [6], macroscopic properties of materials depend on structures and interactions at the atomic and molecular level. From this fact one can draw a conclusion that relationships between various macroscopic properties within a class of materials such as polymers should exist. Following this line of thinking, a relationship between brittleness B and linear isobaric thermal conductivity of polymers α_L has been represented by an equation [7]. Brittleness has been defined in 2006 as follows [8]:

$$B = 1/[\varepsilon_b \cdot E'] \qquad (2)$$

Here ε_b is the tensile elongation at break at a specified temperature T while E' is the storage modulus at the same temperature. All polymers are viscoelastic - while dynamic mechanical analysis (DMA) seems to be the best method of separation of viscous flow (liquid-like) contribution to mechanical properties from elastic (solid-like) contributions. In DMA one applies a sinusoidal load to the material and follows the mechanical material response with time. This technique is also called Dynamic Mechanical Thermal Analysis (DMTA). The solid-like contribution to the overall behavior is represented by the storage modulus E' while the liquid-like contribution is represented by the loss modulus E". There is an entire book by Kevin Menard on DMA [9]. Good descriptions have been provided by Lucas and her colleagues [10] and by Gedde [11].

We note that the connection between B and α_L formulated in [7] pertains to a mechanical property on one side and a thermodynamic one on the other side. This fact encouraged us to seek one more such relationship, namely between flexibility Y and thermal conductivity λ.

2. Relating polymer flexibility to thermal conductivity

We have used the polymer flexibility Y values collected in [2]; the Y units used are $cm^3/[g \cdot kJ]$. For the same materials we have thoroughly searched the literature for reliable thermal conductivity λ values; the units here are $W/[m \cdot K]$.

We have then plotted the values of λ as a function of Y; see Figure 1.

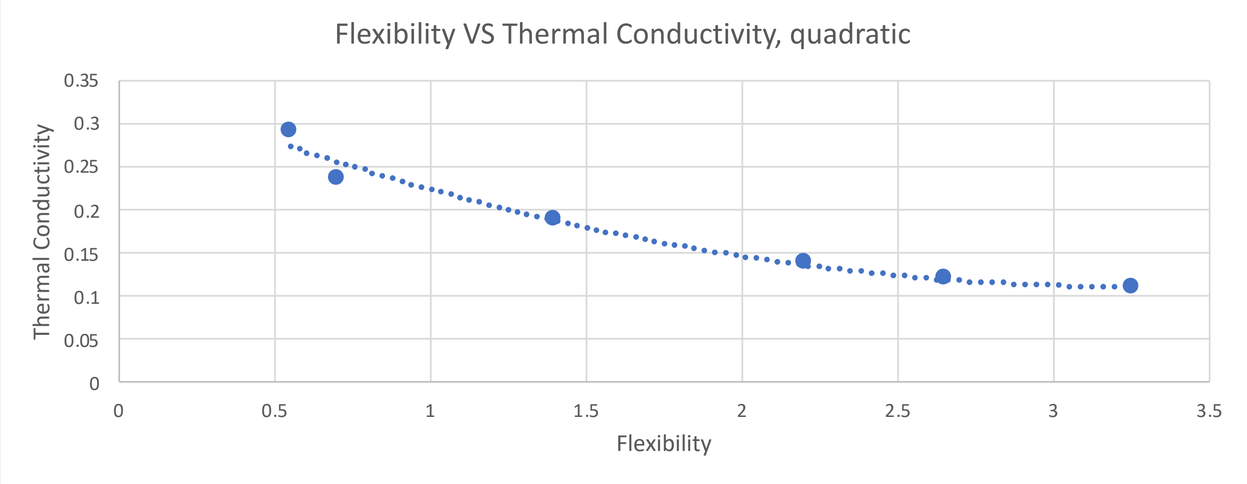

Figure 1. Thermal conductivity as a function of flexibility of polymers.

Figure 1 demonstrates the existence of an unequivocal relationship between λ and Y. That relationship can be represented by an equation:

$$\lambda = 0.3462 - 0.1435Y + 0.0291Y^2 \qquad (3)$$

The goodness of the fit is provided by the parameter $R^2 = 0.975$, with $R^2 = 1$ representing a perfect fit. Since each pair of Y and λ values comes from two different worldwide laboratories, the fit is remarkable.

Needless to say, Eq. (3) can be used 'both ways'. Thus, for materials for which thermal conductivity values are available but flexibility data are not, the equation can be used to calculate Y.

3. Discussion

A possible way of explaining the results reported above is in terms of free volume v^f. It can be defined [12] as

$$v^f = v - v^* \qquad (4)$$

All quantities in the last equation can be expressed in cm^3/g. Here v is the specific volume, the inverse of mass density; v* is the incompressible volume, one can imagine it as the volume at 0 K under a very high pressure so that the free volume is fully "squeezed out". v* can be calculated given v(T) data, or else v(T, P) data where P is the pressure. One uses an equation of state such as v(T) developed by Hartmann and Haque [13] which involves reduced parameters. A set of experimental v(T) data is represented by the equation of state involving reduced volume and reduced temperature:

$$\tilde{v} = v/v^*; \quad \tilde{T} = T/T^* \qquad (5)$$

One thus obtains v* and T*, the former is then used in Eq. (4).

Consider the situation when we are increasing the free volume v^f in a polymer. The chain segments – as well as the entire chains – have more space to move, hence the flexibility increases. The free volume increase means also lower thermal conductivity - since thermal energy transmission takes place via atoms rather than via empty spaces. It is this decrease of λ with increasing Y that we are seeing in Figure 1.

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