Flexibility of Polymers Defined and Related to Dynamic Friction

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Abstract

We have quantitatively defined flexibility of polymers. Flexibility Y is not an inverse of the brittleness B, rather, the two equations are compared. The expression for flexibility includes the specific volume and the summation of the strengths of chemical bonds-a concept introduced by Linus Pauling. The flexibility is plotted as a function of dynamic friction, resulting in a representative single curve for polymers.

Keywords: Polymer Brittleness, Polymer Flexibility, Polymer Dynamic Friction, Strength of Chemical Bonds, Linus Pauling

1. Scope and Definitions

Polymers are characterized in terms of a variety of properties, including "brittleness" and "flexibility". Such characterizations help one to choose a polymer for a specific application. For instance, Wang and coworkers (2018) declare that "flexible materials are very attractive because of easy integration into various industrial processes". They have created polymer-containing composite films "feasible to act as self-powered wearable devices by utilizing body's heat or other heat source to generate electricity, wearable temperature sensors, and flexible solid-state coolers, which are very difficult to achieve for inorganic thermoelectric materials since they are intrinsically brittle and rigid". However, in order to better navigate among intrinsic material properties and to find materials with suitable combinations of properties, an equation defining polymer brittleness B has been formulated by two of us and Narkis (Brostow, Hagg Lobland, & Narkis, 2006), and B has been related to several other properties (Brostow & Hagg Lobland, 2017). By contrast, there has been no quantitative definition of polymer flexibility, call it Y. We provide such a definition in this paper.

Let us mention a few more examples of the importance of Y. Chinaglia and coworkers (2007) developed much improved light-emitting devices, putting green phosphor compounds in a conductive polymer blend; flexibility is a requirement in such devices. Rubbers and rubber-like materials are known for high flexibilities. Yu and Selvadurai (2007) note that large strains can be achieved in rubbers with little energy dissipation while large deformations of a polyurea elastomer were studied by Amirkhizi and coworkers (2006). Relaxation times of chains in polymers studied through molecular dynamics simulations by Bedrov, Liu and Colby (2008) are important for the polymer properties-and necessarily related to flexibility. Dong-Yu Kim and coworkers (2008) have created organic solar cells on flexible polymeric substrates—with much better mechanical properties than ITO (indium tin oxide) solar cells. Polymer based energy storage devices developed by Nyholm and coworkers at the University of Uppsala (2011) require flexible polymers. Being able to predict and quantify the flexibility of such polymeric materials would improve the ease of development of novel flexible materials as well as create a clear method for comparison of the materials.

As mentioned before, flexibility is *not* an inverse of brittleness. We first provide a definition of brittleness *B* (Brostow, Hagg Lobland, & Narkis, 2006) so as to contrast it with the definition of flexibility later:

$$B = \frac{1}{E' * \varepsilon_b} \qquad (1)$$

Here E' is the storage modulus determined by dynamic mechanical analysis at the frequency 1.0Hz and ε_b is the tensile elongation at break. Thus, the equation for brittleness accounts for both fatigue from repetitive loading as well as the strength associated with a large one-time deformation. Since the time of the original definition, B has become connected to several other mechanical and also tribological properties (Brostow & Hagg Lobland, 2017). We assume that flexibility is significantly related to the specific volume V_{sp}. That volume consists of the hard-core volume V* (the sum of volumes of the individual atoms) and the free volume V_f (the remaining volume, increasing with the temperature) (Brostow, 2009):

$$V_{sp} = V^* + V_f \tag{2}$$

All quantities in Eq. (1) pertain to 1 g. While certain properties might be related to the chain length, our consideration of the volume per 1 g should eliminate that effect. We also recall the concept and implications of the strength of chemical bonds defined decades ago by Linus Pauling (1932). The stronger are the bonds inside of a polymer segment, the lower the flexibility. We assume that the chemical bonds between segments do not affect Y significantly. We are now ready to define flexibility of polymers as follows:

$$Y = \frac{V_{sp}}{\sum_i^n U_{bi}} \tag{3}$$

Here V_{sp} is the specific volume in cm³/g at a given temperature while $\sum_i^n U_{bi}$ is the sum of the strengths of bonds in the monomer of a given polymer. We have taken into account that the larger V_{sp} is, the more space there is between the chains, thus enabling their movements and reorientation. The summation in the denominator in Eq. (3) follows the ideas of Pauling; clearly strong bonds provide low flexibility. Being able to predict and quantify the flexibility of polymeric materials would improve the ease of development of novel flexible materials as well as create a clear method for comparison of the materials.

Comparing Eqs. (1) and (3) we see that they do not have even one common parameter. In other words, we have not assumed a simple relationship between Y and B.

2. Connection to Dynamic Friction

A definition of a physical property ought to be useful. The capability to calculate some other property from our flexibility would demonstrate usefulness. A large sector of publications on polymers deals with their mechanical properties. This is understandable; if a material breaks into pieces easily, its other properties are irrelevant. However, as concluded in the so-called Jost report commissioned by the Government of the United Kingdom many decades ago (1966), industry and the entire society incur every year large financial losses when machinery parts have to be replaced by identical ones because of *wear resulting from friction*. For this reason, we focus now on dynamic friction z (often called "coefficient of friction" or "COF"). This parameter is defined as the ratio of the friction force to the applied normal force to maintain a movement at a constant speed. There is also static friction - typically higher and needed to initiate the movement. As discussed by Burris and Sawyer (2009), the definition of z is disarmingly simple - while there are practical challenges in accurate measurements of this quantity.

While in many situations one aims to achieve *low* friction values, Majidi and his colleagues (2006) declare: "High-friction, low-adhesion materials are important for applications such as automobile tires and shoes. Since surface roughness limits contact area, soft materials have typically been used to obtain high friction". A group at the University of California Berkeley used friction to determine directional adhesion of arrays of angled microfibers—inspired by geckos (2008). A group at the University of Toronto (2015) has developed composites with *high* friction on wet ice. Thus, they have created a promising material for ice traction.

In a highly flexible material, we can imagine 'ploughing in' of the probe into the material and the resulting high friction. Consider the polymers widely used in a variety of industries, also in medicine and in food packaging - often called engineering polymers. Given those wide uses, reliable data was available. In other words, if for whatever reason somebody would obtain for a widely used polymer a value much different from that reported in the literature, the experiment would be repeated. Still, literature data for each polymer were within a certain range; this applies to both specific volume and dynamic friction. Therefore, these ranges are marked in the Figure below.

We have plotted Y vs. z values for those polymers for which extensive and mutually consistent values were available. The results are shown in Figure 1; an evident relationship is demonstrated. The results are well represented by a two-parameter equation:

$$Y = 0.311z^{-0.987} \tag{4}$$

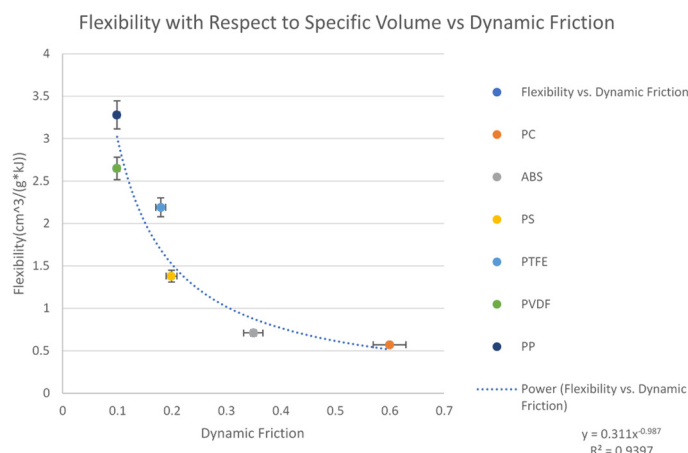Flexibility with Respect to Specific Volume vs Dynamic Friction

Figure 1. A plot of flexibility Y versus dynamic friction z for polymers

We see that polypropylene (PP) has the highest value of flexibility Y and also the lowest value of dynamic friction. The following one is poly (vinylidene fluoride) (PVDF). The next one is polytetrafluoroethylene (PTFE) - well known under the industry name Teflon ® precisely because of low z and a relative ease of manufacturing. The following ones are polystyrene (PS) and acrylonitrile/butadiene/styrene (ABS), the latter an elastomer copolymer. The last one is polycarbonate (PC).

3. General Comments

As mentioned, work on lowering friction and mitigating tracks created by the moving intenter in polymers is pertinent. Such tracks have been studied in some detail (Brostow et al., 2007). Low friction—and low wear related to it—are important also in movable devices in aerospace systems investigated by Voevodin and his colleagues (1999). Different approaches are used to lower polymer dynamic friction, such controlled phase separation developed by Burris, Sawyer and their coworkers in polymer blend thin films (2006). A technique called friction transfer has been developed and applied to deposition of ordered conjugated polymer nanowires and transistor fabrication (Li, Newsome, Russell, Kugler, & Ishida, 2005). Let us also note pattern-directed self-organization in polymer thin films achieved by Grolman and her colleagues (2017). They point out that "many of nature's surfaces have distinct textures on different surfaces of the same object". Nature creating "brick and mortar" structure in nacre became an inspiration for creating such structures in fiber-reinforced polymer composites (De Luca, Sernicola, Shaffer, & Bismarck, 2010). Self-limiting layer-by-layer assembly of well aligned inorganic platelets in a polymer provides a coating with an unusually high stress dissipation capability. Addition of carbon nanotubes to polymers (Giri, Das, & Kalra, 2012) is likely to affect the flexibility. Piezoresistive metal + polymer composites show high stress sensitivity (Kazemian Abyaneh, Ekar, & Kulkarni, 2010)-which might be related to flexibility. Self-organization was mentioned before—while there is an entire book by Desai and Kapral on self-organized and self-assembled structures (2009).

Polymers in contact with liquid or vapours can undergo swelling—a process important in certain applications (Brostow, 1971; Svagan, Hedenqvist, & Berglund, 2009). Our z might possibly serve also as a measure of the degree of swelling. Additive manufacturing of polymers becomes more and more used (Dudek and his colleagues, 2017). Evaluation of flexibility necessarily involving several layers so deposited might be a tool for verification of uniformity of the polymers so created.

Our concept of flexibility applies to continuous polymers. While porous polymers and polymer foams are interesting and have important applications (Haibach, Menner, Powell, & Bismarck, 2006; Kulygin & Silverstein, 2007; Silverstein, 2014), our definition is not directly applicable to them. An interesting phenomenon is polymorphism—seen in various kinds of materials, from inorganic (Lallancette & coworkers, 2018) to polymers (Azzurri, Flores, Alfonso, Sics, Hsiao, & Baltá-Calleja, 2003). Given Eq. (3), it would be interesting to determine changes in flexibility during polymorphic transitions of polymers.

Polymer science has several faces - as shown by Gedde in his book (2001) and by Lucas and her colleagues in their book (2001). While many laboratories are creating valuable experimental data, our philosophy is: by creating relationships between different properties, *we save time and effort in experimentation*. A needed property can be

calculated from a different one. Mechanical, thermodynamic and tribological properties of polymers are so considered. The above paper is an example of implementation of this approach. Another example is calculation of the isobaric thermal expansivity of polymers from the brittleness B (Brostow & Osmanson, 2019).

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Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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