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DEPENDENCE OF LINEAR ISOBARIC THERMAL EXPANSIVITY OF POLYMERS ON THEIR FLEXIBILITY

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Abstract. We have obtained an equation for polymers relating their flexibility Y defined in 2019 to the linear isobaric thermal expansivity α_L. This way we have connected quantitatively a thermodynamic property to a mechanical one. The expansivity is important since different materials expand at different rates on the increase of temperature; the same applies to contraction resulting from cooling. Thus, a temperature change can cause disintegration of a composite with *no mechanical force* involved.

Keywords: polymer flexibility, isobaric thermal expansivity, expansivity mismatch.

1. Introduction

Metals have been used for thousands of years, polymers for somewhat more than a century. Polymer Science and Engineering – a part of Materials Science and Engineering – has adopted from Metals Science and Engineering among other definitions of mechanical properties. Thus, following the metals 'route', typically polymers have been characterized in terms of mechanical properties obtained from tensile testing, compressive testing, 3- or 4-point bending. Actually, tensile testing which provides the tensile modulus seems to be the most popular.[1-3]

In practice, polymers were also characterized *qualitatively* using terms such as "brittleness" or "flexibility". In 2006 brittleness was defined by an equation by Brostow, Hagg Lobland and Narkis,[4] namely

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

Here E' is the storage modulus determined by dynamic mechanical analysis (DMA) at 1.0 Hz while ε_b is the elongation at break in tensile testing at a predefined temperature, often 293 K or 298 K. The DMA technique has been explained by Lucas and her colleagues,[5] by Gedde and Hedenqvist[6] and also by Menard and Menard.[7] Traditional testing methods such as those named above pertain to one-time deformations. Such methods are only weakly related to the service conditions - where repetitive application of mechanical forces is typical. Since DMA involves sinusoidal loading at a constant frequency, both fatigue resulting from repetitive loading and a large one-time deformation are accounted for in Eq. (1).

As noted above, the other term used to characterize mechanical behavior of polymers qualitatively was flexibility. Lu and coworkers[8] discuss flexibility as important for polymeric semiconductors used in photovoltaic devices. Metal-polymer interfaces in such devices might be prone to fracture,[9] hence flexibility on the polymer side is pertinent also for that reason.

Low flexibility polymers can undergo matrix cracking under quasi-static loading.[10]

In 2019 an equation for flexibility Y has been provided:[11]

$$Y = V_{sp}/(\Sigma_i^n U_{bi}) \quad (2)$$

Here V_{sp} is the specific volume of a given polymer in cm^3/g at a specified temperature while $\Sigma_i^n U_{bi}$ is the sum of the strengths of bonds in the monomer. The idea of working with the bond strength has been inspired by the seminal work of Linus Pauling.[12]

Given Eq. (2), it is easy to define polymer rigidity R_p, namely[13]

$$R_p = 1/Y \quad (3)$$

Brittleness has been related to several other properties. Already in the literature[4] B was related by an equation to recovery in sliding wear determination – a tribological property. Later on B was related by an equation to the Charpy impact strength and the Izod impact strength[14] and also to thermal expansivity.[15] As stated in the literature,[16] "Brittleness of polymers may also impact the ease and modes of polymer processing, thereby affecting economy of production." We believe that flexibility can also be connected to other polymer properties – mechanical or otherwise. An attempt to create one such connection is described below.

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2. Demonstration of a Relationship

We believe that flexibility is related to free volume v^f. That volume, usually in cm^3g^{-1}, is related to the specific volume V_{sp} in the same units as follows:

$$Vsp = v^* + v^f \quad (4)$$

Here v* is the hard core volume; one can imagine it as the volume per gram at the temperature of 0 K and a pressure so high that the entire free volume has been 'squeezed out'. Consider now a polymeric material in which we would like to increase the flexibility. A natural way to do so is to put in more free volume. In practice, at atmospheric pressure this would be a difficult operation; one can increase v^f by increasing the temperature, but thermal energy increased at the same time would affect many properties.

Linear isobaric thermal expansivity α_L is defined as follows:

$$\alpha_L = L^{-1}(\partial L/\partial T)P \quad (5)$$

Here L is the length of the sample while P is pressure. There exists also volumetric isobaric thermal expansivity α_V which can be calculated from α_L for isotropic materials; the latter is defined as

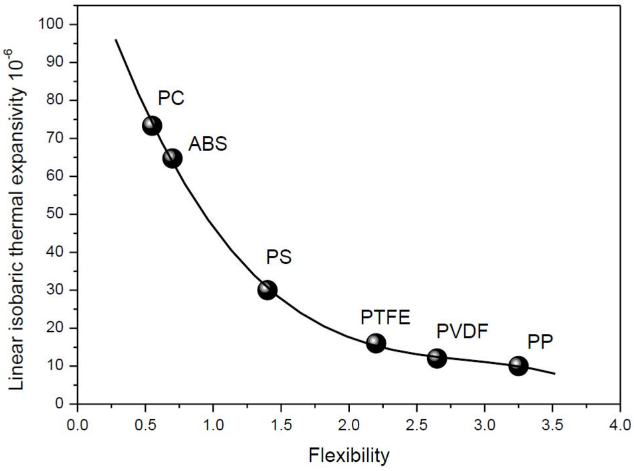
$$\alpha_V = Vsp^{-1}(\partial Vsp/\partial T)P \quad (6)$$

For anisotropic materials three measurements of α_L are needed in three mutually orthogonal (X, Y, Z) directions. α_L is often called "coefficient of linear thermal expansion" even though already Lord Kelvin in 1890 noted that the word "coefficient" provides no information.[17] A good method of determination of α_L is thermomechanical analysis (TMA) – well described by Lucas,[5] by Gedde and Hedenqvist[6] and also by Brostow and Hagg Lobland.[18]

Isobaric thermal expansivity is important in composites since typically each constituent of a composite has its own values of α_L and α_V. Increasing the temperature can easily result in separation of composite constituents because of α_L mismatch. Thus, a temperature change ΔT causes disintegration of a composite with *no mechanical force* involved. If we have $\Delta T < 0$, the disintegration might occur as well. Cases are known of fairly large structures disintegrating under a temperature change.

Given the importance of thermal expansivity, one wonders whether it could be related to flexibility. Consider an experiment in which we increase the temperature a little to determine αL. Atoms and chain segments gain more space for their movements. Consider the scenario in which there is low free volume, hence low flexibility. Now atoms and chain segments hit the surrounding atoms, increasing free volume and increasing Y. Now consider a second case when v^f is high and Y is high. Now collisions between atoms are less frequent and weaker. A small temperature increase will affect the free volume only little, hence the change in flexibility will be small too. We infer that low flexibility corresponds to high expansivity – and *vice versa*.

To verify this hypothesis, we have collected α_L vs. Y for widely used polymers - widely used because of their advantageous properties. For instance, PTFE is used because of its high thermal stability, strong chemical resistance, low friction, and good self-lubrication.[19] Polycarbonate (PC) is used because of its stability, durability and transparency.[20] From left to right, we show in Fig. points for polycarbonate, acrylonitrile-butadiene-styrene (ABS) copolymer, polystyrene (PS), polytetrafluoroethylene (PTFE, Teflon), poly(vinylidene fluoride) (PVDF) and polypropylene (PP).



Linear isobaric thermal expansivity α_L as a function of flexibility for important engineering polymers

As we see in Fig. 1, our hypothesis is confirmed. The curve in the Figure is represented by an equation:

$$\alpha_L = 124.2 - 110.44Y + 37.21Y^2 - 4.32Y^3 \quad (7)$$

The goodness of the fit is represented by the parameter R^2, with $R^2 = 1$ corresponding to the perfect fit. Parameters in Eq. (5) correspond to $R^2 = 0.999$. As noted above, we have used highly reliable values – but each from a different laboratory. Our R^2 parameter is remarkable.

3. Concluding remarks

Flexibility of polymers has been considered for a long time as important for specific applications. Begovic and his colleagues in Belgrade and Novi Pazar created D layered flexible coordination polymer structures without interconnectivity between individual polymer layers.[21] Vempati and Natarayan[22] created flexible polymer microtubes and microchannels via electrospinning. Laskarakis and coworkers[23] created hybrid (inorganic–organic) polymer materials deposited onto flexible polymeric substrates. Such materials provide sufficient barrier response against oxygen and water vapor penetration. Sinha and coworkers[24] used laser to induce graphene onto lignin-upgraded flexible polymer matrix. Jiang and coworkers[25] demonstrated than one can create non-planar polymer-based flexible electronics fabricated by a four-axis additive manufacturing process. Flexible composites of graphene coated with a CaSiO3/acrylic polymer membrane were studied by Gomez-Solis and coworkers at the University of Guanajuato.[26] When such composites are immersed into a simulated body fluid solution for 21 days, a layer of biocompatible hydroxyapatite is formed.

Linse and Källrot[27] performed Monte Carlo simulations of adsorption of uncharged homopolymers of various flexibilities in good solvent onto planar surfaces with various polymer−surface interaction strengths. The adsorption process was simulated by Brownian dynamics. Flexible polymers adsorbed in two layers, while at an increasing surface attraction the number of adsorbed polymers increased and those polymers become flatter. By contrast, inflexible rod-like polymers adsorbed in a single and thin layer with a nematic-like order. Manterola and coworkers[28] studied adhesives in bonded structures. Degradation of flexible bonded joints exposed to environmental conditions is significantly accelerated when external loads act on them. Hsu and Juan[29] developed an optical methodology for determination of the deflection radius of flexible polymeric substrates. Fan, Weerheijm and Sluys[30] followed deformation-to-fracture evolution of a flexible polymer under split Hopkinson pressure bar loading. Molnár, Virág and Hálasz[31] created a multifunctional apparatus for performing shear and yarn-pull tests of woven fabrics and flexible sheet-like materials. The apparatus can be mounted on a usual ‘universal mechanical testing’ machine. Rivetti and coworkers[32] report results of conformational analysis of DNA molecules with sections of different flexibility. Wunderlich and Grebowicz[33] studied phase transitions of linear flexible macromolecules - and also of liquid crystals, plastic crystals and condis crystals in liquid and glassy phases. Rigidity of liquid crystals is well known. Khokhlov and Semenov[34] applied statistical mechanics to study liquid-crystalline ordering in the solutions of macromolecules with limited flexibility. Dubov and coworkers[35] describe flexible semi-amorphous carbon nitride films with outstanding electrochemical stability derived from soluble polymeric precursors. They are usable in photoelectronics and photocatalysis and apparently flexibility is pertinent.

From a broader perspective, we note the statement by Rafael Balart and his colleagues at the Polytechnic University of Valencia and at the University of Perugia:[36] “In the last decade, continuous research advances have been observed in the field of environmentally friendly polymers and polymer composites due to the dependence of polymers on fossil fuels and the sustainability issues related to plastic wastes.”

Author Contributions

Data curation, Nora Hamad; Investigation, Haley E. Hagg Lobland and Nora Hamad; Writing – original draft, Witold Brostow; Writing – review & editing, Witold Brostow and Haley E. Hagg Lobland. The authors declare no conflict of interests.

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ЗАЛЕЖНІСТЬ ЛІНІЙНОЇ ІЗОБАРНОЇ ТЕРМІЧНОЇ РОЗШИРЮВАНОСТІ ПОЛІМЕРІВ ВІД ЇХНЬОЇ ГНУЧКОСТІ

Анотація. *Отримано рівняння для полімерів, яке пов'язує їхню гнучкість Y, визначену в 2019 році, з лінійною ізобарною термічною розширюваністю* α_L. *Таким чином ми кількісно пов'язали термодинамічну властивість з механічною. Розширюваність важлива, оскільки різні матеріали розширюються з різною швидкістю з підвищенням температури; те ж саме стосується і стиснення в результаті охолодження. Отже, зміна температури може спричинити дезінтеграцію композиту без застосування механічної сили.*

Ключові слова: *гнучкість полімеру, ізобарна термічна розширюваність, невідповідність розширюваності.*