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Brittleness and toughness of polymers and other materials

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ABSTRACT

Materials are often characterized in terms of their toughness, though more than one definition of toughness exists. Likely the most widely recognized means of defining material toughness, denoted here as τ, is by the area under the stress strain curve from a tensile test. Another important feature describing the nature of materials is that property known as brittleness, which has for a long time been much less quantitatively understood. Using a quantitative definition of brittleness provided in 2006, we demonstrate the existence of a quantitative relationship between τ and brittleness B, valid for polymers with a very wide range of chemical structures and properties, for some polymer-based composites, and also for steel and aluminum. We provide an equation relating toughness to brittleness, while for polymers we mark the determining influence of chemical structures on the properties B and τ.

1. Introduction and scope

The concept and measurement of toughness are certainly not new, yet it is apparent that there are undiscovered knowledge and insights on materials toughness that can yet enhance materials research and engineering even in the 21st century with all its technology. The term "materials toughness" is often used, but there are several definitions of that quantity. One of those definitions says that toughness τ is the area under the engineering stress σ vs. engineering strain ε curve determined in tensile testing [1–3]. Thus

$$\tau = \int_0^{\varepsilon_b} \sigma \, d\varepsilon \tag{1}$$

where ε_b is the elongation at break. This is the most often used definition of toughness, although on occasions compression testing has been performed for an analogous purpose. The term "toughness" is also applied to the key result of impact testing, namely the energy necessary to cause fracture at high rates of force application [4,5]. Thus there exists fracture toughness, notch toughness, determined in impact testing for a predetermined geometry of the notch and testing method (e.g. Charpy, Izod), or else drop impact determination. The central feature of toughness has to do with the amount of energy a material can absorb or disperse, in the form of deformation, before it fractures from the imposed stress. Thus we know that toughness is a measure of the energy required to crack a material. Clearly this can be measured in a variety of ways, and one can see that it is particularly important for items that suffer impact; for instance, with a hammer, turbine, etc., strength without toughness yields a poor product. Brittle materials like ceramics that are strong but not ductile have low toughness, while (not necessarily for the same reasons) certain ductile materials having low strength are also not tough.

Since tensile testing toughness is used so often, we have used it (according to Eq. (1)) in the analysis presented here. We expound upon its connection to another mechanical property, namely brittleness B. In 2006 Moshe Narkis and two of us [6] provided the following definition:

$$B = 1/(\varepsilon_b E') \tag{2}$$

Here E' is the storage modulus determined by dynamic mechanical analysis (DMA, also called dynamic mechanical thermal analysis or DMTA) at 1.0 Hz, both at the temperature of interest (in the present case, room temperature). Since formulation of Eq. (2), further materials have been tested and found to fit the correlation, while labs worldwide have utilized the definition of B in various ways and for varied material types; more on this below.

It is worth noting that already a clear correspondence between the viscoelastic recovery of polymers and brittleness has been identified; a correspondence that enables the prediction of brittleness from scratch testing [6]. Likewise a connection between the impact strength of materials and their brittleness has already been shown [7]. The demonstration of a trend of decreasing impact strength with increasing brittleness, along with comments to

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us by peers about the relationship between material toughness and B, led us to further investigation. The significance is highlighted by the fact that material toughness is a term applied to materials as diverse as silk [8], bioinspired ceramics [9], and metallic glasses [10]. Here we focus primarily on polymer-based materials, although a couple metals have also been tested, suggesting the possible universality of the discovered connection.

Before moving to the experimental design and results, consider that ductility is represented in Eq. (2) by the ε_b term. Strength is represented by the E' term, important also because it comes from repetitive sinusoidal loading [11]; repetitive loading—and fatigue possibly resulting from it—must be taken into account in design for many service conditions. It is essential to understand that for plastics, the strength of a material can be unrelated to average properties such as elastic modulus. On the other hand, microscale deformation is likely the more important determining factor of toughness [12]. Considering copolymers styrene acrylonitrile (SAN) and acrylonitrile butadiene styrene (ABS) as illustrative examples, one finds that tensile elongation signifies a material's capacity to deform before breaking and is therefore a more important design factor than many of the average properties [12]. Eq. (2) accounts for this in the ε_b term, while the storage modulus accounts for elasticity and fatigue.

Literature provides us with various pieces of information useful for our purpose.

Keten and coworkers explain the strength of silk in terms of uniformity of strain distribution in nanocrystals—provided the size of the nanocrystals does not exceed 3 nm [8]. Somewhat similarly, Bouville and his colleagues [9] note the importance of several size scales for mechanical properties. The descriptor B turned out to be useful in evaluating polymer blends [13], multi-layer laminate composites [14] and composites of vulcanized polymer blends with a shock-resistant ceramic [15]. In the case of blends studied [13], the rates of change of ε_b and E' were different, thus affecting the outcome in B with changing concentration of components. B decreases when a rigid copolymer is added to linear low-density polyethylene [13]. The study of multilayer composites by Chen and coworkers at the University of Sichuan [14] shows among other things that B is inversely proportional to structural integrity of laminate multiphase composites; apparently B reflects also adhesion between the laminate layers. In polymer+shock-resistant ceramic composites, B is much reduced [15] by chemical treatment of the ceramic filler particles that improves their adhesion to the matrix. The results reported in [8,9,14,15] confirm the decisive role of interfaces for properties of multiphase materials [16–20], including porous ones [21].

2. Experimental data used

In our work on brittleness [6,7,22,23] we have worked with polymers, polymer-based composites, and some metals. The number of materials has gradually enlarged as we have scanned the literature for reliable data (beyond what we ourselves generated); thus the experimental data now used come from a variety of sources. Materials included are the following: Al =aluminum; UH=ultra-high molecular weight polyethylene; PPSU=polyphenylsulfone; PCL=polycaprolactone; PP=polypropylene; Santoprene=Santoprene^{TM} (trade name of an elastomer); PC=polycarbonate; LDPE=low-density polyethylene; Surlyn=Surlyn 8149 (ethylene/methacrylic acid copolymer); PVDF=poly(vinylidene fluoride); PTFE=polytetrafluoroethylene; ABS=acrylonitrile/butadiene/styrene; PES=polyethersulfone; PMMA=poly(methylmethacrylate); SAN=styrene/acrylonitrile copolymer (trade name Luran); PS=polystyrene.

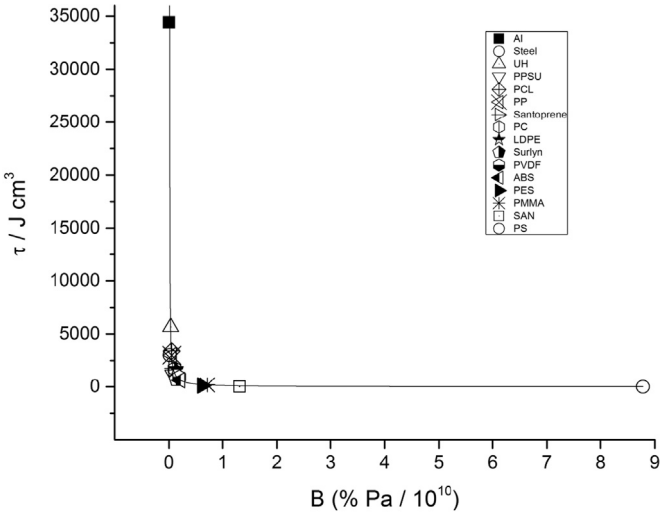

Fig. 1. Toughness τ vs. brittleness B for a variety of materials. The solid line corresponds to the best fit given by Eq. (3).

3. Results and discussion

The expected relationship between τ and B is presented graphically in Fig. 1. While we focus on polymers, steel and aluminum are included as well.

In Fig. 1 we see significant "crowding" of points in the middle part of the diagram. Therefore, in Fig. 2 we present the middle part of the diagram.

We find in both figures a one-to-one relationship between toughness (Eq. (1)) and brittleness (Eq. (2)). We have represented that relationship by the following equation:

$$\tau = (b + cB)/(1 + aB) \tag{3}$$

The parameters a, b and c are "universal" constants, although they are necessarily dependent on the temperature. The continuous lines in Figs. 1 and 2 have been calculated from Eq. (3) with $a=-111$, $b=-14102$ and $c=-1640$. The goodness of fit parameter $R^2=0.934$. We recall that the experimental data come from a variety of sources. With all data from a single laboratory, one would expect the R^2 parameter to be even higher.

Dirk Van Krevelen and coworkers have developed methods of prediction of several properties of polymers on the basis of their

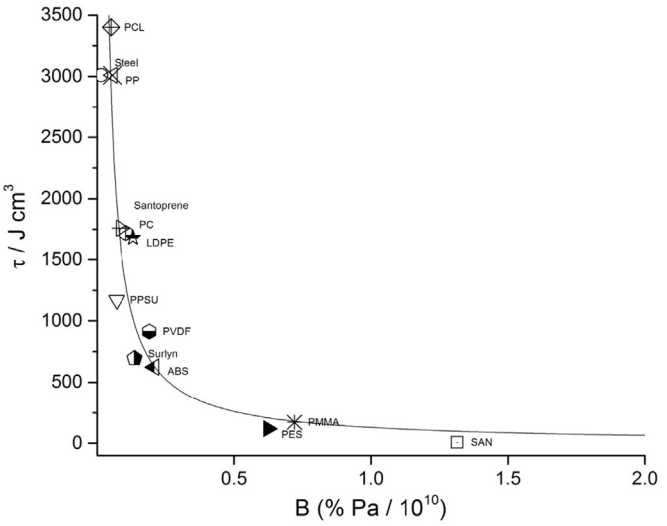

Fig. 2. Expanded view of the middle part of the toughness vs. brittleness diagram. The solid line corresponds to the best fit given by Eq. (3).

chemical structures [24]. Such concepts are used in synthesis of new polymers [25]. Microstructures of polymers are related to toughening brittle polymers [26] and to brittle-to-tough transition when increasing the temperature [27]. Thus, in the tough state of polypropylene–ethylene copolymers one observes only isolated deformation structures (croids or cavitation bands) [27]. Importantly, whatever is the structure of a material at several levels and the resulting mechanical and tribological properties, that structure is reflected in the brittleness values. For example, the unusually high value of B and low value of τ for polystyrene seen in Fig. 1 are both consequences of flat and rigid phenyl rings in polystyrene. In another instance, the structure and morphology of polymer composites containing poly(butylene succinate-co-adipate) (PBSA) and polystyrene plus titania (TiO_2) fibers are affected by varying the concentration of TiO_2 an effect borne out by changes in brittleness. Pure PS fibers dramatically increase the brittleness as expected; they also lower the Young modulus. Addition of increasing amounts of TiO_2 to the fibers has the opposite effect, that is brittleness lowering [28].

4. Concluding remarks

As briefly mentioned above, we have also obtained two further equations, one relating B to the Charpy impact strength and the other to the Izod impact strength [7]. Thus, the choice "should we use the stress vs. strain diagram or the impact strength to characterize material toughness" has lost its edge. Now τ as defined by Eq. (1) is related to B, and so are both kinds of impact strength.

Earlier we demonstrated a quantitative relationship represented by an equation between B and viscoelastic recovery in sliding wear determination [6]. That recovery is explained in a review article [29]. The connection reported in [6] thus relates a mechanical property to a tribological one, while tribological properties of materials including wear are increasing in importance for both technical and economical reasons [30,31].

Mechanical properties of polymers are more difficult to deal with than those of metals and ceramics; viscoelasticity with its time dependence of properties constitutes a severe complication [20]. Now our Eq. (3) makes possible the calculation of one more important mechanical property on the basis of known brittleness values, at least for polymers. A goal for future work is to expand the number and type of polymer-based materials tested and to explore the relationships as a function of varied temperatures and other test parameters; further analysis of metals could be pursued through collaboration. By showing the relationship between τ and B, and earlier between two kinds of impact strength and B, we provide extensive knowledge while needing only a relatively small amount of experimentation. Such knowledge could be especially valuable in setting expectations for outcomes of material design modifications. When a polymer is reinforced by a filler, sometimes combined with functionalization of that filler [32], the magnitude of reinforcement achieved can be evaluated quantitatively.

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