J Mater Sci (2010) 45:242–250
DOI 10.1007/s10853-009-3926-5

Brittleness of materials: implications for composites and a relation to impact strength

Witold Brostow · Haley E. Hagg Lobland

Received: 16 July 2009 / Accepted: 23 September 2009 / Published online: 8 October 2009

Abstract Brittleness of materials—whether it occurs naturally or with aging—affects significantly performance and manifests itself in various properties. In the past, brittleness was defined qualitatively, but now a definition of brittleness for viscoelastic materials exists, enabling analysis of all types of polymer-based materials. The quantity brittleness, *B*, has been evaluated for neat thermoplastics, but here composites and metal alloys are also assessed. The physical significance of brittleness is connected to the dimensional stability of materials. The connections of brittleness to tensile elongation and to fatigue are explored while its relationship to surface properties—specifically wear by repetitive scratching—is examined more closely. The economic impact of wear results in monetary loss associated with failure and reduced service life of plastic parts—thus its connection to brittleness finds use across a broad spectrum of industrial applications which utilize plastics for manufacturing, processing, etc. We also demonstrate a correspondence between impact strength (Charpy or Izod) and brittleness of polymers. It is shown that the assumption hardness is equivalent to brittleness is inaccurate; this fact has important implications for interpreting the results of mechanical testing of viscoelastic materials.

Introduction and scope

Brittle materials are frequently encountered, whether expected or not. In the case of polymers, some are by nature brittle while others become brittle due to environmental conditions or aging. Embrittlement of polymers with aging is commonly observed and is reported in the literature [1–4]. Similarly, metals and ceramics are also discussed in terms of brittleness. Clearly, the notion of brittleness is not new; rather it is a significant concept in all of materials science and engineering. The creation of composite materials is one way to avoid the problem of brittleness; a variety of studies report on the changes in mechanical properties of polymers reinforced with fillers including fibers, nanotubes, and others [5–7]. Other options for modifying polymers include fluorination [8], fluoropolymer additives to fluorless polymers [9, 10], intentional synthesis of multiphase systems [11], nanocomposite formation [12], and/or special processing such as in supercritical carbon dioxide [13].

Manuscripts from a 1974 symposium on toughness and brittleness of plastics [14] provide a collection of knowledge regarding brittle behavior of polymer-based materials (PBMs) and different factors which contribute to its manifestation. Despite this, the quantity *brittleness* was defined largely by the visual assessment of fractures and related properties. For example, Yee et al. [15] report the ductile-to-brittle transition by changes in the strain behavior and by electron micrographs of the fracture surfaces. The authors provide no quantitative measure of brittleness allowing direct comparison of one material to another.

This work was presented at POLYCHAR 17 World Forum on Advanced Materials, April 20–24, 2009, in Rouen, France.

W. Brostow · H. E. Hagg Lobland (✉)
Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science & Engineering, University of North Texas (UNT), 1155 Union Circle #305310, Denton, TX 76203-5017, USA
e-mail: haleylobland@gmail.com
URL: Website: http://www.unt.edu/LAPOM/

W. Brostow
e-mail: brostow@unt.edu

A significant concept related to brittleness is presented by Matsuoka [16]: using styrene acrylonitrile copolymer (SAN) and acrylonitrile butadiene styrene copolymer (ABS) as examples, Matsuoka describes how for plastics the strength of a material can be *unrelated to average properties* such as elastic modulus. On the other hand, *micro-scale deformation* appears more important in determining toughness. Matsuoka writes, "Tensile elongation indicates the ability of a material to deform before breaking; it is a more important design factor in choosing a proper material than many of the average properties…" [16]. Later Menges and Boden [17] also reported on the significance of the relationship between elongation and brittleness.

Further progress in understanding brittleness and toughness of polymers includes a 1992 article by Wu [18] that links chemical composition and chain structure to toughness, where toughness is determined by impact testing; we note that there are several definitions of toughness. Similarly Mikos and Peppas describe in several articles between 1988 and 1991 [19–22] their development of models connecting polymer chain entanglement and molecular weight to fracture behavior. Among others, the work by Menges and Boden, Wu, Mikos and Peppas offers reasons for the occurrence of so-called brittle fracture in certain cases.

An index of brittleness proposed by Quinn and Quinn [23] in 1997 was developed for ceramics. Quinn and Quinn's selection of parameters, however, assumes a material will behave elastically—an assumption clearly *not* applicable to viscoelastic PBMs and also of limited applicability to other materials. Consequently, there has remained until recently a demand for a quantitative description of brittleness in general and in particular for PBMs, as at least four decades of previous work had not produced a usable and widely applicable definition. This is in spite of the fact that the term "brittleness" has been used repetitively to describe materials behavior [24, 25].

We published such a definition in 2006 [26]. That equation for brittleness (B) is

$$B = 1/\varepsilon_b E' \qquad (1)$$

where ε_b is the tensile elongation at break and E' is the storage modulus as determined by dynamic mechanical analysis (DMA). The relevance of ε_b to brittleness has already been discussed. Use of the storage modulus accounts for the viscoelastic nature of polymers. Since brittle behavior arises from the solid-like rather than liquid-like behavior of PBMs, the storage modulus (at a selected frequency of 1.0 Hz) is appropriate here. The inverse relationship described by Eq. 1 was further validated in 2008 [27].

Furthermore, calculated values of B have been connected to other properties such as wear and free volume [26, 27]. There exists evidence that different classes of properties should be related to each other [28–30], and that idea is founded on the fact that all properties result from the structure and interactions for a given material [31]. On this basis we have demonstrated connections between tribological and electrical properties [28], among others. Specifically, a connection between electric conductivity and friction has been demonstrated [28] from identification of the percolation threshold (with conductivity analysis similar to that in [32]). It is on the same basis that in the present paper a quantitative connection between brittleness and impact resistance is sought. An important reason for defining such links is to gain the capacity to predict performance and properties based on one or a few other properties. This can be especially important for tribological properties (i.e., wear and friction) that are not always tested but play a significant role in the service life of PBMs [33].

The question of whether Eq. 1 applies not only to neat polymers [26, 27], but also to PBMs containing metal or ceramic particles is addressed in the present study. We expect that it will hold even for different kinds of fillers, blends, or hybrids as the parameters ε_b and E' should be sensitive to changes resulting from such modifications—as seen for instance in nanocomposites described by Broza et al. [5].

Experimental procedures

Materials

The polymeric materials selected for analysis come from different classes of thermoplastic polymers and possess a variety of chemical structures and mechanical properties. All of the polymers used were standard unfilled injection-molding grade polymers; they are listed in Table 1 along with abbreviations and manufacturer information. Materials numbered 1–13 were reported also in previous publications [26, 27]. Specimens of these were prepared by injection molding, compression molding, or provided in sheets by the supplier. Amorphous polymers include PC, PS, SAN, ABS, PES, and PPSU. The semi-crystalline materials are PP, PTFE, Surlyn, LDPE, PVDF, and PMMA. Santoprene, as a thermoplastic elastomer containing EPDM (ethylene propylene diene monomer) rubber and polypropylene, contains crystalline and amorphous phases. Additionally from among this set are homopolymers (PC, PS, PES, PP, LDPE, PMMA) and copolymers (SAN, ABS, Santoprene, Surlyn), fluoropolymers (PTFE, PVDF), and sulfone-containing polymers (PES, PPSU). Furthermore, the materials represent different rigidity schemes, for instance: PVDF is a relatively soft semicrystalline fluoropolymer, PMMA is semicrystalline and

Table 1 List of materials studied with abbreviations and manufacturer information or description (for composites and metal alloys)

	Material	Abbreviation	Manufacturer/description
1	Polycarbonate	PC	Dow Chemical Company
2	Polypropylene	PP	Huntsman
3	Polystyrene	PS	Aldrich Chemicals Company
4	Polytetrafluoroethylene	PTFE	Dow Chemical Company
5	Styrene/acrylonitrile copolymer (Luran®)	SAN	BASF
6	Santoprene™	Santoprene	Advanced Elastomer Systems
7	Acrylonitrile/butadiene/styrene	ABS	Dow Chemical Company
8	Surlyn® 8149 (ethylene/methacrylic acid copolymer)	Surlyn	E.I. du Pont de Nemours
9	Polyethersulfone	PES	Solvay Engineered Plastics
10	Low-density polyethylene	LDPE	Huntsman
11	Poly(methylmethacrylate)	PMMA	RTP Company
12	Polyphenylsulfone	PPSU	Solvay Advanced Polymers, L.L.C.
13	Polyvinylidene fluoride	PVDF	Solvay Solexis, Inc.
14	Hytrel®	Hy	E.I. du Pont de Nemours
15	Hytrel + aluminum	HyAl	(10% aluminum nanopowder)
16	Polycaprolactone	PCL	Solvay
17	Polycaprolactone + silica	PCL-SIL	(10% silica micropowder)
18	Ultrahigh molecular weight polyethylene (UHMWPE)	UH	Ticona
19	UHMWPE + white graphite	UHWG	(2% white graphite micropowder)
20	Copolyester	CBDO	Proprietary
21	Steel	Steel	(314 stainless steel)
22	Aluminum	Al	(6061 alloy)

hard (also known as Plexiglas in the Americas and as Perspex in Europe), while PPSU is amorphous, hard, and very heat and chemicals resistant. Each is a commonly used engineering thermoplastic.

Materials numbered 14–22 include several polymer composites in addition to neat polymers. These polymer and polymer composite specimens were prepared by compression molding: the HyAl and PCL-SIL materials were first blended in a C.W. Brabender D-52 Preparation Station, while the UHWG sample was mixed by ultrasonication in methanol followed by drying to remove excess solvent. Hytrel is a block copolymer thermoplastic elastomer composed of rigid poly(butylene-terephthalate) (PBT) and flexible poly(tetramethylene oxide) (PTMO). Aluminum flakes added to the Hytrel [34, 35] had an average diameter of 125 nm. The biodegradable polyester polycaprolactone had nonbranching chains resulting in a semicrystalline material. The silica added to it had an average particle size of 4.1 μm.

As its name shows, UHMWPE differs from other polymers in the unusually high molecular weight—what makes the material viscous even at elevated temperatures and thus difficult to melt and mold. White graphite was added at 2% by weight and appears as 5–15 μm bundles of platelets (not shown) within the UH matrix. The term white graphite refers an undisclosed experimental material provided by a company with the agreement that its identity shall not be revealed. The material is similar to graphite only in its ability to be used as a solid lubricant. The polymer CBDO is a co-polymer, specifically the co-poly-terephthalate) of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) described in a paper by Beall et al. [36].

Steel and aluminum alloys, materials numbered 21 and 22 in Table 1, were machined into the appropriate specimen shapes for testing. The alloys selected are commonly used types of steel and aluminum.

Calculation of brittleness values

Values of B were calculated according to Eq. 1. Data for the storage modulus E' was collected from Dynamic Mechanical Analysis (DMA) using the three-point-bending apparatus at frequency 1.0 Hz. The DMA technique has been well described by Gedde [37], Lucas et al. [38], and also by Menard [39, 40]. Specimens were run through a temperature scan from −15 °C to 60 °C at 5 °C/min. The amplitude of deflection was maintained at 5 μm at the start of each run by adjusting the static and dynamic loads, with the static force always 10% higher than the dynamic force. The reported values of E' (Table 2) are for the temperature 25 °C.

For materials numbered 1–13, ε_b values were collected from the MatWeb Online Materials Database

Table 2 Tabulated values of brittleness B and recovery f (in sliding wear) along with data used to calculate brittleness (elongation at break ε_b and storage modulus E')

	Material	ε_b/%	E'/Pa	B (% Pa/10^{10})	f/%
1	PC	97.90	9.66E+08	0.106	51.44
2	PS	6.90	1.65E+08	8.783	29.61
3	PTFE	400.00	6.67E+07	0.375	50.57
4	SAN	4.00	1.90E+09	1.316	46.56
5	Santoprene	525.00	2.18E+08	0.087	80.48
6	ABS	27.30	8.26E+08	0.443	51.06
7	Surlyn	325.00	2.23E+08	0.138	67.57
8	PES	30.20	5.30E+08	0.625	51.74
9	LDPE	190.00	4.00E+08	0.132	84.49
10	PP	120.00	9.66E+08	0.056	67.30
11	PMMA	4.50	3.08E+09	0.722	79.43
12	PVDF	35.00	1.49E+09	0.192	86.40
13	PPSU	120.00	2.20E+09	0.038	66.15
14	Hy	1229.76	9.87E+07	0.082	83.75
15	HyAl	797.24	1.39E+08	0.090	85.44
16	PCL	806.61	2.41E+08	0.051	79.69
17	PCL-SIL	914.66	3.13E+08	0.035	77.38
18	UH	406.02	7.66E+08	0.032	54.13
19	UHWG	404.30	6.91E+08	0.036	56.21
20	CBDO	121.70	9.29E+08	0.088	51.00
21	Steel	45.59	3.61E+10	0.006	53.49
22	Al	18.52	3.51E+10	0.015	23.06

(http://www.matweb.com). The reported values are averages for the neat, unfilled polymers. For materials numbered 14–22—which contain composite and hybrid materials prepared in-house—ε_b was determined by tensile testing on an 810 Material Test System (MTS Systems Corporation). Standard dog-bone shaped specimens were prepared in compliance with ASTM standards: ASTM E 8 for the metal samples; and ASTM D 638 Type IV specimens for the polymer materials (excluding Hy and HyAl which were Type V). Reported values (Table 2) are averages from five runs; data for the neat polymers were in agreement with averages in the MatWeb database.

Sliding wear

Sliding wear tests, described in [10, 41], were conducted by the same method described in [26] and [27]. The sliding wear behavior was evaluated on a micro-scratch tester (MST) (with a Rockwell diamond tip, 200 µm radius) from CSM Instruments, Neuchatel, Switzerland. A test consisted of 15 scratches by the diamond tip along the same groove; each was conducted at room temperature (~25 °C) with a sliding speed of 5.0 mm/min over a length of 5.0 mm. Sliding wear tests were performed under constant loads of 5.0, 10.0, and 15.0 N (three runs at each force). The penetration depth R_p (instantaneous depth of penetration) and residual depth R_h (depth after recovery time of 2 min) were measured at the midpoint (2.5 mm) of the scratch grooves.

From the depth data the percentage of viscoelastic recovery f for the 15th scratch was calculated according to the following equation defined in [10]:

$$f = \left[\frac{(R_p - R_h)}{R_p}\right] \cdot 100\% \qquad (2)$$

Impact resistance

Values of the Charpy impact strength and Izod impact strength were collected from the Matweb Online Materials Database (http://www.matweb.com). The data are averages for notched specimens. Due to limited availability of data, values are not reported for all materials for which B was calculated. Plotting and curve fitting were conducted with OriginLab. In order of least to highest brittleness, materials in Fig. 3a are UH, PPSU, PC, PTFE, ABS, PES, SAN, and PS; likewise materials in Fig. 3b are PPSU, PC, LDPE, Surlyn, PTFE, PES, PMMA, SAN, and PS.

Brittleness and sliding wear

The brittleness values of the materials listed in Table 1 are depicted in Fig. 1 on a one-dimensional scale. We find that most of the PBMs are clustered at the low end of the scale. Materials with higher brittleness include SAN, PMMA, and PES along with ABS and PTFE in the middle range. As shown before when the definition Eq. 1 was first formulated [26], polystyrene possesses the highest value of brittleness among the tested materials. Anyone who has worked with polymers is also familiar with this by experience, that PS without modification is extremely brittle. On the other hand, the metal alloys have comparatively low brittleness. It is expected that neither stainless steel nor aluminum should be very brittle, given the very large storage modulae of aluminum and steel. Values of the elongation-at-break for PBMs in different rigidity schemes are normalized by specimen size and testing speed while the standards for tensile testing of metals demand larger specimens and typically slower testing speeds (i.e. rate of extension) that are comparable to what is used for rigid polymer specimens. Further, it is now evident that the brittleness scale can be used not only for neat polymers but also for other PBMs such as composites and hybrids containing ceramic and metal particles.

An important outcome of the definition of brittleness is its physical significance: the lower the brittleness, the

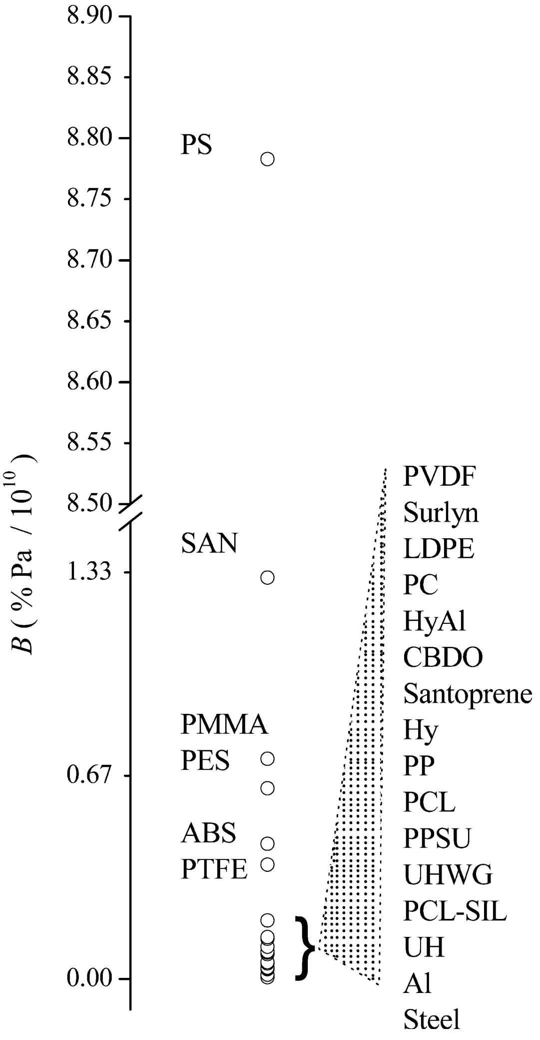

Fig. 1 Scale of brittleness for polymers and metals, with B calculated according to Eq. 1

higher the dimensional stability of the material in service in repetitive loading. To spell it out: the storage modulus E' determined by *dynamic* mechanical analysis addresses the repetitive (fatigue) component; ε_b takes care of a large load which (in contrast to DMA) does not immediately convert into a load of equal size but in the opposite direction. Interestingly, thus far our definition of brittleness has not been applied to ceramics for the reason that it is difficult or impossible to obtain values of ε_b for these materials. Therefore, the index developed by Quinn and Quinn [23] can be applied to ceramics while the scale defined by our Eq. 1 fills a gap in the present knowledge of brittleness as it applies to polymers and possibly also to metals.

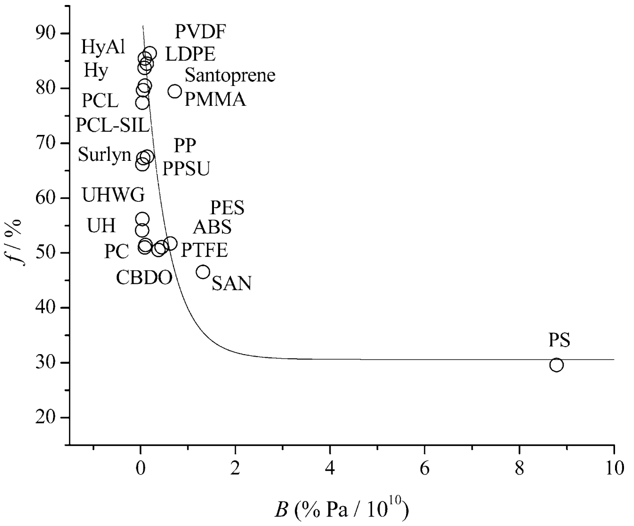

Fig. 2 The percentage of viscoelastic recovery as a function of brittleness for all materials (excluding metals). The *solid line* represents an exponentially decaying function defined by Eq. 3 fit to the experimental data points

As mentioned in the “Introduction”, tribological properties—especially wear—have a large impact on the performance and service life of PBMs. For this reason the capacity to predict the wear behavior of a material is very valuable. Using the calculated brittleness values and the results of sliding wear tests for each of the materials shown in Fig. 1, we have found an exponential relationship between the two. That connection is shown in Fig. 2, a plot of the percentage of viscoelastic recovery in sliding wear versus the brittleness; the results can be represented by the equation

$$f = 30.6 + 67.1e^{-B/0.505} \tag{3}$$

here the viscoelastic recovery has been defined [10] by Eq. 2.

It is important to recognize that for metals the recovery in scratch testing is *elastic* in nature. This is plainly evident since the predicted B values for Steel and Al are for higher recoveries than what is observed. This difference corresponds to the *viscous* component, present in the case of polymeric materials.

The relationship between viscoelastic recovery, f, in sliding wear (multiple scratching along the same groove) and B assumes that the PBMs undergo strain hardening [26, 27, 40–44]. All the polymeric materials tested and shown in Figs. 1 and 2 were found to undergo strain hardening. On the contrary, there is little strain hardening in sliding wear for the metals under the same test conditions. Plastic deformation and defect propagation may prevent toughening of the scratch groove in crystalline metals such as stainless steel and aluminum.

While a mechanism for strain hardening in polymers is often densification [44], the mechanism for work hardening in metals is naturally different. In polymers, multiple passages of the indenter result in pushing macromolecular chains to the sides and also down below the surface of the groove, hence densification. This explanation has been confirmed by nanohardness determination [45] for polyethylene and polypropylene. As a result of densification, nanohardness inside the groove increases after multiple passages of the indenter. In polystyrene, because of its high brittleness as discussed above, consecutive indenter passages result mostly in debris formation while nanohardness inside the groove *decreases*. Polycarbonate shows still different behavior: the indenter just plows the material aside without debris formation or densification. Nanohardness inside and outside the groove are in PC practically the same. Thus, in PE, PP, and PC sliding wear testing results in permanent groove formation without debris formation. Clearly the old measure of wear in terms of debris weight—developed originally for metals—is useless for such polymers.

The strain induced by repetitive scratching may cause either work hardening or work softening in metals. A report by Rigney [46] reveals that for amorphous metals a decrease in density accompanied by increased free volume led to work softening. Elsewhere Rigney suggested that simple crystalline metals were more likely to work harden under sliding wear type conditions, however, this was not universally true for all crystalline metals [47].

The results of Rigney for metals indicate a correspondence between higher free volume v^{f} and low brittleness—similar to that demonstrated by us for polymers in 2006 [26]. The free volume v^{f} is essentially the sum of all unoccupied space in a given specimen. Based on the time–temperature correspondence of polymer properties [48], we know that one can observe property changes at higher temperatures (higher v^{f}) that would take years or decades to occur if at lower temperatures (lower v^{f}). The free volume is defined [49] as

$$v^{\mathrm{f}} = v - v^{*} \tag{4}$$

where volumes are usually in $\mathrm{cm}^3\ \mathrm{g}^{-1}$, v is the total specific volume, and v^* is the incompressible (hard core) volume. The free volume can be imagined as what would be “squeezed out” of a real material by cooling it down to 0 K while simultaneously applying an infinitely high pressure. Foundational to using Eq. 4 is an equation of state of the form $v = v(T, P)$, where T is the thermodynamic temperature and P is pressure. Others have shown [48, 50–53] that one can obtain reliable predictions—for a variety of PBMs with different types of phases—for decades of years by using in particular the Hartmann equation of state [54]

$$\tilde{P}\tilde{v}^5 = \tilde{T}^{3/2} - \ln\tilde{v} \tag{5}$$

the reduced parameters are defined as follows:

$$\tilde{v} = v/v^*; \quad \tilde{T} = T/T^*; \quad \tilde{P} = P/P^* \tag{6}$$

Comparability of different materials is improved by using hard-core or reducing parameters (v^*, T^*, P^*) [49, 54], while the concept of reduced variables goes back to 1870 or so in the work of van der Waals. Litt [55] first derived the $\tilde{T}^{3/2}$ dependence of $\tilde{v}$ based on theoretical calculations; Hartmann later added the $\tilde{P}\tilde{v}^5$ term based on a large body of empirical data—on both crystalline and glassy (amorphous) polymers—showing the pressure dependence of $\tilde{v}$ [54]. Hartmann and Haque explained and demonstrated the validity of Eq. 5 for amorphous polymers existing above and below the glass transition temperature. Therefore, Eq. 5 can be applied even to polymers such as PS, PC, and PES which at room temperature are below the glass transition. Thus, the main concern in properly determining v^* from the Hartmann equation of state is to take account of the thermal history in glassy polymers. Zoller and Walsh [56] report a sizeable list of $v(T, P)$ data. Applying Eq. 5 to that data, v^*, T^*, and P^* were obtained; and then using Eq. 4, values for the free volume were determined. Incidentally, Eq. 5 works also for molten polymers, but obviously with different values of v^*, T^* and P^* than in the solid state.

Note further that our comparison of a wide range of material types is not dependent on all the materials exhibiting the same type of fracture. We know that the brittle-to-ductile transition is defined as the temperature at which 50% of specimens undergo ductile fracture and 50% undergo brittle fracture by impact testing [57]. An alternate description is that above the transition there is sufficient free volume to give ductile fracture while below it the smaller free volume yields brittle fracture. Obtaining the values E' and ε_{b} does not require that all materials be tested at a temperature within a defined region of a particular mode (ductile or brittle). On the contrary, the two parameters are measured at the same temperature thereby permitting the comparison of different materials existing under similar environmental conditions.

Brittleness and impact strength

It is clear from this discussion that brittleness ought to be related to impact resistance. The two most common measures of that resistance are the Charpy impact energy (U_{C}, mostly used in Europe) and the Izod impact energy (U_{I}, mostly used in the US). For Charpy one reports the breaking energy per unit of cross-sectional area; for Izod the breaking energy per unit of specimen thickness at the breaking point. The Izod test is inherently less accurate than the Charpy test because the specimen geometry in the former is not symmetric (half of the specimen inside a vise, half out) while in the latter there is symmetry with respect to the center of the tested specimen. Both methods are described for instance by one of us [58].

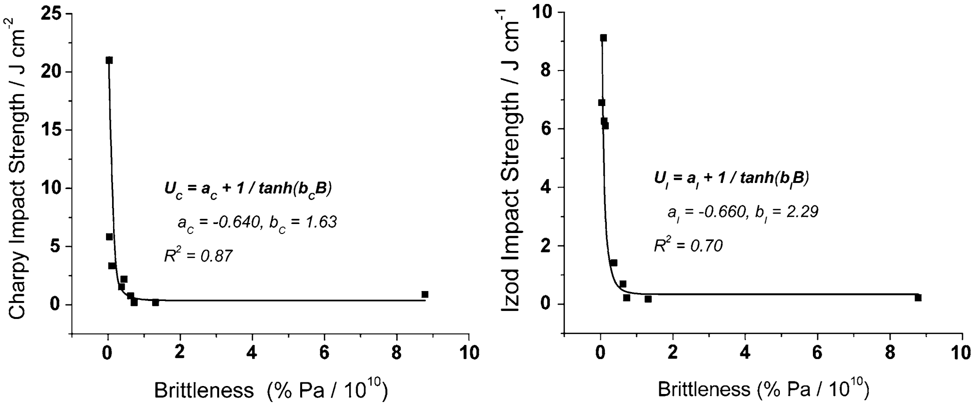

Fig. 3 Charpy and Izod impact strength versus brittleness for a subset of materials (defined in the "Experimental" section). The *solid lines* correspond to the best fit given by Eqs. 7 and 8

Figure 3 shows the impact strength plotted as a function of brittleness for Izod and Charpy testing, respectively. The data points in the figures have been represented by the equations

$$U_C = a_c + 1/\tanh(b_C B) \tag{7}$$

$$U_I = a_I + 1/\tanh(b_I B) \tag{8}$$

where values of the parameters a_C etc. are given in the figures. Based on the nearly flat shape of the curves for high x-values, we observe that when $B > 1$, then a further increase in B does not bring about any further lowering of U_C or U_I. Any material thus offers some resistance to impact, even a very brittle one.

The best fit curves are defined by R^2 values of 0.87 for the Charpy data and 0.70 for the Izod data. Recall that values for the impact strength and elongation at break were averages from an online database. Thus, R^2 equal to 0.87 is good and reasonable for the Charpy impact strength versus B plot. The lower accuracy of the Izod technique, as mentioned before, contributes to the smaller R^2 value for the fit shown in Fig. 3. A better fit would presumably require an improvement in the experimental techniques. When one of us developed a theory of ductile–brittle impact transition temperature [57], the definition already noted was: the temperature at which 50% of specimens fail in a brittle way and the rest in ductile way. Thus, even specimens from one batch are not expected to behave in an identical way. The recent progress seems to be in providing supposedly significant digits by the software rather than in the sample preparation or the experiment design accuracy. Thus, $R^2 = 0.87$ might well be "in the nature of the beast".

Survey of results

In our discussion the importance of the time-dependent nature of polymer properties has been highlighted. The aspect of time-dependence has been acknowledged in recent articles suggesting new methods of *dynamic* nano-indentation [59, 60]. The results from nano-indentation are not yet widely understood or connected to other known properties. In fact, quite a few elastic modulus results obtained from nano-indentation experiments are wrong. Oliver and Pharr [60] developed a method to obtain the modulus by nano-indentation for materials which are *fully elastic*. However, the method has been applied to a variety of materials which do not fulfill that condition. Research groups in various countries [61–63] have demonstrated that large errors result from using the Oliver and Pharr method outside of its legitimate application range. Of course this does not invalidate the nano-indentation technique, only some of the values calculated from it; used correctly, the technique is well-regarded.

In a study on nano-indentation of PMMA, Morel and Jardret [64] conclude that brittle behavior in the scratch may be connected to tensile behavior. This is interesting in that it supports our use of a tensile parameter ε_b in the definition of brittleness Eq. 1. However, in their conclusion, Morel and Jardret use hardness as a stand-in for brittleness. Our own sliding wear tests clearly indicate that hardness is not equivalent to brittleness. Moreover, the problem of a number of distinct methods of evaluation of hardness would constitute another complication if following the route of Morel and Jardret. There exists some relationship between hardness and *penetration depth* (in sliding wear). So-called 'hard' materials are typically penetrated less; but we have found no clear correlation between R_p and *brittleness*.

Considering tribology, both single scratch testing and sliding wear can provide information about the viscoelasticity and wear of polymers. Connecting these to mechanical properties gives a better understanding of how the bulk properties influence surface behavior. Furthermore, the definition of brittleness formulated in 2006 [26] is simple, predictive, and applicable to a wide range of materials. Still further, Eq. 1 it is functional—an advantage for users.

In our calculation of B, we have used ε_b values from tables and from individual tests. Therefore, if such data are available, one needs only to calculate E' from DMA by 3-point-bending, a test requiring only small amounts of material in an easily attained sample shape. Additionally, others can more readily execute sliding wear tests at a constant load, a method less sensitive than progressive load tests (which are significantly affected by the different capacities of equipments to precisely control the force).

A wide range of polymers—within the categories of thermoplastics and thermoplastic elastomers have been examined in this work. While the chemical crosslinks in thermosets strongly affect chain mobility and viscoelasticity, the underlying dependence on free volume remains the same for thermosets as for thermoplastics.

Given the wide variety of materials analyzed, we are mindful that the definition of brittleness formulated allows comparison of a range of materials. Importantly, we are able to compare numerous polymers without regard to their differing glass transition temperatures. The properties evaluated are dependent on the free volume—which in turn depends on temperature [48, 65]—for both thermoplastics and thermosets. Therefore, we have a baseline characteristic of different classes of materials under the same, easily obtained, environmental conditions.

We have found that adding ceramic particles to a polymer matrix may change the brittleness of the pure polymer. The change—whether an increase or decrease—depends on multiple factors (particle dispersion, filler-matrix adhesion, the amount of filler added, etc.), and typically (but not always) the tensile elongation is reduced for polymer–ceramic composites. Ceramics are recognized as brittle materials, with most exhibiting little or no measurable elongation before break in tensile testing. Indeed, from more than 6000 ceramic materials in the MatWeb database only 72 have values for ε_b, and most of those are not pure ceramics. High values for E' are expected while their combination with very low elongations at break should result in relatively high values of B for ceramics.

Strain rate sensitivity is a concern in comparing vastly different classes of materials. This concern applies for comparison of polymers with either ceramics or metals. To see any tensile elongation in ceramics, the extension rate must be very slow (less than 1.0 mm/min). Because there are different contributing mechanisms for polymers and ceramics, an analysis of the latter could be undertaken to determine the outcome of brittleness according to Eq. 1.

While connections between brittleness and behavior in scratch testing (scratch resistance, sliding wear) have been to a varying extent explored before [26, 27], the connections of B to impact testing parameters, U_C and U_I, has been first demonstrated above. This constitutes one more proof of the usefulness of our definition of B—in all kinds of applications for properties and performance assessment—and also supports our philosophy of looking for connections between ostensibly different quantities characterizing materials.

Acknowledgements The authors thank the Robert A. Welch Foundation for funding (Grant # B-1203) and the US Department of Defense for a National Defense Science and Engineering Graduate Fellowship (to H.E.H.L.).

References

1. Fiebig J, Gahleitner M, Paulik C, Wolfschwenger J (1999) Polym Test 18:257
2. Ho CH, Vu-Khanh T (2004) Theor Appl Fract Mech 41:103
3. Wilson KV Jr, Smith BL, Macdonald JM, Schoonover JR, Castro JM, Smith ME, Cournoyer ME, Marx R, Steckle WP Jr (2004) Polym Degrad Stab 84:439
4. Schwarz I, Stranz M, Bonnet M, Petermann J (2001) Colloid Polym Sci 279:506
5. Broza G, Kwiatkowska M, Roslaniec Z, Schulte K (2005) Polymer 46:5860
6. Bunsell AR, Renard J (2005) Fundamentals of fibre reinforced composite materials. CRC Press, Boca Raton, FL
7. Bismarck A, Mohanty AK, Aranberri-Askargorta I, Czapla S, Misra M, Hinrichsen G, Springer J (2001) Green Chem 3:100
8. Ho T, Wynne KJ (1992) Macromolecules 25:3521
9. Brostow W, Cassidy PE, Hagg HE, Jaklewicz M, Montemartini PE (2001) Polymer 42:7971
10. Brostow W, Bujard B, Cassidy PE, Hagg HE, Montemartini PE (2002) Mater Res Innov 6:7
11. Janik H, Palys B, Petrovic ZS (2003) Macromol Rapid Commun 24:265
12. Amir N, Levina A, Silverstein MS (2007) J Polym Sci Chem 45:4264
13. Sun H, Cooke RS, Bates WD, Wynne KJ (2995) Polymer 46:8872
14. Deanin RD, Crugnola AM (eds) (1976) Brittleness and toughness of plastics. American Chemical Society, Washington, DC
15. Yee AF, Olszewski WV, Miller S (1976) In: Deanin RD, Crugnola AM (eds) Toughness and brittleness of plastics. American Chemical Society, Washington, DC
16. Matsuoka S (1976) In: Deanin RD, Crugnola AM (eds) Toughness and brittleness of plastics. American Chemical Society, Washington, DC
17. Menges G, Boden H-E (1986) In: Brostow W, Corneliussen RD (eds) Failure of plastics. Hanser Publishers, Munich
18. Wu S (1992) Polym Int 29:229
19. Mikos AG, Peppas NA (1988) J Chem Phys 88:1337
20. Mikos AG, Peppas NA (1989) J Mater Sci 24:1612. doi: 10.1007/BF01105680
21. Mikos AG, Peppas NA (1989) J Mater Sci Lett 8:833
22. Mikos AG, Peppas NA (1991) J Polym Sci B Polym Phys 29:837
23. Quinn JB, Quinn GD (1997) J Mater Res 32:4331
24. Werwa E (2000) J Mater Educ 22:18
25. Hagg Lobland HE (2006) J Mater Educ 28:29
26. Brostow W, Hagg Lobland HE, Narkis M (2006) J Mater Res 21:2422
27. Brostow W, Hagg Lobland HE (2008) Polym Eng Sci 48:1982
28. Brostow W, Keselman M, Mironi-Harpaz I, Narkis M, Peirce R (2005) Polymer 46:5058
29. Brostow W, Narkis M, Olea-Mejia O (2004) ANTEC annual technical conference of the society of plastics engineers, Society of Plastics Engineers, Chicago
30. Brostow W, Chonkaew W, Menard KP (2006) Mater Res Innov 10:389

31. Brostow W (1979) Science of materials. Wiley, New York
32. Nogales A, Broza G, Roslaniec Z, Schulte K, Šics I, Hsiao BS, Sanz A, García-Gutiérrez MC, Rueda DR, Domingo C, Ezquerra TA (2004) Macromolecules 37:7669
33. Brostow W, Deborde J-L, Jaklewicz M, Olszynski P (2003) J Mater Educ 24:119
34. Brostow W, Gorman BP, Olea-Mejia O (2007) Mater Lett 61:1333
35. Brostow W, Buchman A, Buchman E, Olea-Mejía O (2008) Polym Eng Sci 49:1977
36. Beall GW, Powell CE, Hancock J, Kindinger M, McKenzie HR, Bray AV, Booth CJ (2007) Appl Clay Sci 37:295
37. Gedde UW (2001) Polymer physics. Kluwer, Dordrecht
38. Lucas EF, Soares BG, Monteiro E (2001) Caracterização de Polimeros e-papers, Rio de Janeiro
39. Menard KP (2000) In: Brostow W (ed) Performance of plastics. Hanser, Munich-Cincinatti
40. Menard KP (2008) Dynamic mechanical analysis—an introduction. CRC Press, Boca Raton, FL
41. Brostow W, Damarla G, Howe J, Pietkiewicz D (2004) e-Polymers 025:1
42. Bermudez MD, Brostow W, Carrion-Vilches FJ, Cervantes JJ, Damarla G, Perez MJ (2005) e-Polymers 003:1
43. Bermudez MD, Brostow W, Carrion-Vilches FJ, Cervantes JJ, Pietkiewicz D (2005) e-Polymers 001:1
44. Brostow W, Chonkaew W, Rapoport L, Soifer Y, Verdyan A (2007) J Mater Res 22:2483
45. Brostow W, Chonkaew W, Mirshams R, Srivastava A (2008) Polym Eng Sci 48:2060
46. Rigney DA, Fu XY, Hammerberg JE, Holian BL, Falk ML (2003) Scripta Mater 49:977
47. Rigney DA (2000) Wear 245:1
48. Brostow W (2001) In: Brostow W (ed) Performance of plastics. Hanser, Munich–Cincinnati
49. Flory PJ (1985) Selected works. Stanford University Press, Stanford, CA, USA
50. Brostow W, D'Souza NA, Kubát J, Maksimov R (1999) J Chem Phys 110:9706
51. Akinay AE, Brostow W (2001) Polymer 42:4527
52. Akinay AE, Brostow W, Castaño VM, Maksimov R, Olszynski P (2002) Polymer 43:3593
53. Akinay AE, Brostow W, Maksimov R (2001) Polymer 41:977
54. Hartmann B, Haque MA (1985) J Appl Phys 58:2831
55. Litt MH, Tobolsky AV (1967) J Macromol Sci Phys 1:433
56. Zoller P, Walsh D (1995) Standard pressure–volume–temperature data for polymers technomic. Lancaster, PA
57. Brostow W (2000) In: Brostow W, Corneliussen RD (eds) Failure of plastics. Hanser, Munich
58. Brostow W (2007) In: Mark JE (ed) Physical properties of polymers handbook. Springer, NY
59. Beake BD, Bell GA, Brostow W, Chonkaew W (2007) Polym Int 56:773–778
60. Oliver W, Pharr G (1992) J Mater Res 7:1564
61. Rau K, Singh R, Goldberg E (2002) Mater Res Innovat 5:151
62. Tho KK, Swaddiwudhipong S, Lui SZ, Zeng K-Y, Hua J (2004) J Mater Res 19:2498
63. Alkorta J, Martines-Esnaola JM, Gil-Sevillano J (2005) J Mater Res 20:432
64. Morel P, Jardret V (2002) Mater Res Soc Symp Proc 710:DD7.7.1-6
65. Brostow W (2009) Pure Appl Chem 81:417