DEFINITION OF BRITTLENESS: CONNECTIONS BETWEEN MECHANICAL AND TRIBOLOGICAL PROPERTIES OF POLYMERS

Haley E. Hagg Lobland, B.S., M.S.

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APPROVED:

Witold Brostow, Major Professor
Rick Reidy, Committee Member and Chair of the Department of Materials Science and Engineering
Dorota Pietkewicz, Committee Member
Nigel Shepherd, Committee Member
Costas Tsatsoulis, Dean of the College of Engineering
Sandra L. Terrell, Dean of the Robert B. Toulouse School of Graduate Studies

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The increasing use of polymer-based materials (PBMs) across all types of industry has not been matched by sufficient improvements in understanding of polymer tribology: friction, wear, and lubrication. Further, viscoelasticity of PBMs complicates characterization of their behavior. Using data from micro-scratch testing, it was determined that viscoelastic recovery (healing) in sliding wear is independent of the indenter force within a defined range of load values. Strain hardening in sliding wear was observed for all materials—including polymers and composites with a wide variety of chemical structures—with the exception of polystyrene (PS). The healing in sliding wear was connected to free volume in polymers by using pressure-volume-temperature (P-V-T) results and the Hartmann equation of state. A linear relationship was found for all polymers studied with again the exception of PS. The exceptional behavior of PS has been attributed qualitatively to brittleness. In pursuit of a precise description of such, a quantitative definition of brittleness has been defined in terms of the elongation at break and storage modulus—a combination of parameters derived from both static and dynamic mechanical testing. Furthermore, a relationship between sliding wear recovery and brittleness for all PBMs including PS is demonstrated. The definition of brittleness may be used as a design criterion in selecting PBMs for specific applications, while the connection to free volume improves also predictability of wear behavior.

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CHAPTER 1

SCOPE

Polymer-based materials (PBMs)—as bulk materials and thin films—are highly valued and used in wide variety of applications. With increasing frequency, metal parts are being replaced by polymeric ones.[1] Several reasons for this trend are that PBMs are easy to process, lightweight, easy to maintain and relatively inexpensive.[2] This means, for instance, more mileage per gallon for cars and airplanes due to lighter weight vehicles. However, a shift toward increased use of polymeric materials demands advancements in polymer science and engineering (PSE), especially with regard to wear of PBMs.

Tribology—formally defined as the "science and technology of interacting surfaces in relative motion and of related subjects and practices"—deals with wear, friction, abrasion, and lubrication.[3] The importance of tribology cannot be understated. In his 1995 book on friction and wear, Rabinowicz [4] refers to the 1966 Jost report which estimated losses due to ignorance of tribology at M£ 515 per year in Britain. Rabinowicz wrote:

> At the time the Jost Report appeared it was widely felt that the Report greatly exaggerated the savings that might result from improved tribological expertise. It has now become clear that, on the contrary, the Jost Report greatly underestimated the financial importance of tribology. The report paid little attention to wear, which happens to be (from an economical point of view) the most significant tribological phenomenon.[4]

While external lubricants have long been used as a straightforward and fairly effective method to reduce wear for metal parts,[4] due to not infrequent swelling of polymers in contact with liquid lubricants, the approach cannot simply be transferred. It has been shown [5] that carbon black in polymer blends results in lower friction in both irradiated and un-irradiated samples. However, in certain applications the accompanying lack of transparency and black color may be disallowed. In another instance, I have shown [6,7] that addition of a fluoropolymer to an epoxy resin reduces friction and improves scratch resistance at certain blend compositions. These are specific examples where the knowledge of polymer tribology is being advanced.

Nonetheless, the growth in replacing metals with PBMs has not been matched by a similar growth in the understanding of polymer tribology. This is evidenced by the lack of literature on tribology of such materials. This persists—with some improvements during the last several years—despite development of many new techniques for creating heterogeneous composites and nanohybrids [8,9] among others [10]. In books [11-13] that focus on PBMs, mechanics is covered well while the words "friction" and "wear" cannot be found in the indices. Furthermore, from the literature we find that those groups with expertise in mechanics hardly venture into tribology. Even in a book on engineering tribology [14], only one of sixteen chapters is devoted to non-metallic materials; and that is split further to discuss both polymers and ceramics.

We know at least one reason why the tribology of polymers is not more advanced: it is a difficult area. In particular, while metals and ceramics are elastic materials, polymers are viscoelastic. This complicates analysis of PBMs because it means there is a *time-dependence* of properties. For instance, viscoelastic effects on the occurrence of different surface features during scratch testing have been described.[15,16] In fact, most tribological models are based on the behavior of metals [3], and that is largely due to the extensive groundwork—including scratching and wear of metals and ceramics—laid out by Bowden and Tabor in the 1950's and 60's.[17,18] There has not yet been a comparable amount of work presented on the tribology of polymer-based materials.

In the area of tribology, the scratch test has found widespread use during recent decades.[19-24] It is useful for tribological testing not only of polymer coatings [22,25-27] but also of bulk polymers.[28-34] The introduction of scratches can compromise the integrity of coatings and affect performance. The impact of a scratch on material performance is really dependent on the type and extent of damage that occurs during scratching. Therefore, understanding the wear behavior of polymers is key to enabling wider use of PBMs in applications where surface properties play a critical role. The types of damage incurred to polymers as a result of scratching include plowing, ironing, cutting, and fragmentation.[28] Cutting and fragmentation are also classified as wear. Wong and coauthors state that the cause of each type of damage depends on the mode of deformation, ductile or brittle or both.[28] The idea of brittleness is an important concept to which we shall return.

In spite of recent increases in reports on polymer tribology, there remains still a lack of fundamental knowledge and therefore lack of predictability that stand as obstacles to developing new PBMs with lower wear. Given the need for new tribological investigations and the already well-defined presence of polymer mechanics, I decided to connect the two. A basis for exploring such connections is the following: since all macroscopic properties are dependent on molecular structure and interactions,[35] we can expect therefore connections between tribological and mechanical properties. This principle has already been demonstrated. In varied compositions of carbon black-containing polymer blends, the minimum of friction coincides with the minimum of electrical resistivity [5]. Some connections between scratch resistance and the Young's modulus and tensile strength [36] and also with tan δ [37] have been described. Xiang et al. [33] have made attempts to correlate the scratch behavior of bulk polymers to the Young's modulus, yield stress, tensile strength, and also friction coefficient, scratch hardness, and elastic recovery. These efforts move us in the direction of behavior predictions.

A concern in the area of wear and scratch testing is methodology. Wong et al. [32] describe some of the proposed approaches to quantifying scratch resistance. The main difficulty is not how tests ought to be conducted but what parameters should be used to describe the outcome and enable comparability with other results. Reported in this work are commonly recognized and unmodified parameters describing the penetration and residual depths and viscoelastic recovery following sliding wear tests by multiple scratches. Individual tests are conducted under a constant load rather than a progressive one.

There is a variety of methods for wear determination. Some old methods still in wide use rely on measuring the weight of debris. This is an unusually primitive method, and the results depend on how well a brush swept across a worn surface can remove the debris generated. While such methods may suffice at times to evaluate wear, for many PBMs there is often little or no debris formed: material moved by an indenter may be pushed to the sides forming two ridges along the indenter path. The single scratch test and sliding wear test simulate tribological contacts that generate wear. In service in tribological contacts the same location is often 'attacked' repetitively. For these reasons the method of sliding wear determination by repetitive scratching along the same groove has been developed.

Prediction of properties is one goal of this work. As the demands for PBMs rise, the capability to predict properties in advance is increasingly important to avoid trial-and-error product development and to use efficiently time and resources. I describe in this work the development of a definition (or scale) of brittleness of materials based on mechanical properties and its connection to tribological behavior.

Clearly brittleness is not a new idea. In fact it is a familiar and significant concept referred to often in all of materials science and engineering, not just polymer science and engineering. This is very evident in that a symposium, jointly sponsored by the American Chemical Society and the Society of Plastics Engineers, was convened in 1974 to specifically address toughness and brittleness of plastics. A collection of papers from that symposium are published together in a single volume [38]. These manuscripts describe a large body of knowledge regarding brittle behavior of PBMs and different factors which contribute to its manifestation. Despite the large effort expended by the participants of that symposium on the subject of brittleness of materials, the quantity brittleness is defined largely by the visual assessment of fractures and related properties. For instance, Yee et al. [39] report the ductile-to-brittle transition by changes in the strain behavior and by electron micrographs of the fracture surfaces. While the observations and conclusions in the report are valid, there is no quantitative measure of brittleness allowing direct comparison of one material to another.

A key concept related to brittleness is presented by Matsuoka [40] in the same volume of symposium papers. Using SAN (styrene acrylonitrile copolymer) and ABS (acrylonitrile butadiene styrene copolymer) as an example, Matsuoka describes how for plastics the strength of a material can be *unrelated to average properties* such as elastic modulus. By contrast, micro-scale deformation is likely the more important determining factor of toughness. In turn, 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…” Twenty years later, Menges and Boden [41] echo the significance of the relationship between elongation and brittleness.

Since then some progress has been made in the understanding of brittleness and toughness of polymers. Of note is a 1992 article by Wu [42] connecting chemical composition and chain structure to toughness, as determined by impact testing. Along similar lines, a series of articles by Mikos and Peppas between 1988 and 1991 [43-46] describe the development of models to connect polymer chain entanglement and molecular weight to fracture behavior. Along with other published reports, these works provide reasons why we observe so-called brittle fracture in some cases or achieve toughness in others.

In 1997 an index of brittleness was proposed by Quinn and Quinn [47], but it was developed for ceramics. Thus, the brittleness parameter defined by Quinn and Quinn assumed features applicable to ceramics but not necessarily to viscoelastic polymers. Further details of their report will be discussed at more length later. Therefore, in the beginning of my work there was still a need for a quantitative description of brittleness in general and for polymer-based materials. No less than four decades of previous work on the subject have not produced a usable and generally applicable definition.

CHAPTER 2

PHASE 1 – DEFINING THE CONNECTIONS

2.1 Materials

The materials selected for the first phase of this work represent different classes of thermoplastic polymers possessing varied chemical structures and mechanical properties. The materials are listed in Table 2.1 with manufacturer information. Amorphous polymers include PC, PS, SAN, ABS, and PES; while PP, PTFE, Surlyn, and LDPE are semi-crystalline. Some of these materials are hard while others such as PTFE and the elastomer Santoprene along with polyolefins PP and LDPE are softer materials. 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) and copolymers (SAN, ABS, Santoprene, Surlyn), a fluoropolymer (PTFE), and a sulfone-containing polymer (PES). Specimens were prepared by injection molding or provided in sheets by the supplier. All materials were standard unfilled injection-molding grade polymers.

TABLE 2.1. List of materials (Set 1).

Polymer	Abbreviation	Manufacturer
Polycarbonate	PC	Dow Chemical Company
Polypropylene	PP	Huntsman
Polystyrene	PS	Aldrich Chemicals Company
Polytetrafluoroethylene	PTFE	Dow Chemical Company
Styrene/acrylonitrile copolymer (Luran®)	SAN	BASF
Santoprene™	Santoprene	Advanced Elastomer Systems
Acrylonitrile/butadiene/styrene	ABS	Dow Chemical Company
Surlyn® 8149 (ethylene/methacrylic acid copolymer)	Surlyn	E.I. du Pont de Nemours
Polyethersulfone	PES	Solvay Engineered Plastics
Low-density polyethylene	LDPE	Huntsman

2.2 Experimental Procedures

2.2.1 Viscoelastic Recovery in Sliding Wear

Sliding wear tests of all materials listed in Table 2.1 were conducted on a micro-scratch tester (MST) (with a Rockwell diamond tip) from CSM Instruments, Neuchatel, Switzerland. The procedure has been described in the literature [7,48], and is also described further in Section 2.3. A sliding wear test consists of 15 scratches by the diamond tip along the same groove. The materials were tested at room temperature (~25 °C) with a sliding speed of 2.5 mm/min over a length of 5.0 mm. Sliding wear tests were conducted under constant loads of 5.0, 10.0, and 15.0 N.

Reported values of the penetration depth R_p and residual depth R_h were measured at the midpoint (2.5 mm) of the scratch grooves. The percentage of viscoelastic recovery f for the 15th scratch was calculated according to the following equation defined in [7]:

$$f = \left[\frac{\left(R_p - R_h\right)}{R_p} \right] \cdot 100\% \qquad 2.1$$

Equation (Eq.) 2.1 applies to both single scratch and sliding wear tests.

2.2.2 Storage Modulus

Based on dynamic mechanical analysis (DMA),[49,50] the storage E' and loss E'' modulae were determined using a DMA7e machine from Perkin Elmer Co. Specimens were rectangular with nominal dimensions 20.0 x 6.0 x 3.0 mm. A three-point bending geometry was used in the temperature scan mode at frequency 1.0 Hz. To allow comparisons between materials from different rigidity schemes, the static and dynamic forces applied were varied to maintain the starting amplitude at 5 μm for all samples. In all cases, the static force was 10 % higher than the dynamic force. Reported values of E' are for the temperature 25 °C.

In contrast to static testing, in DMA one applies a sinusoidal stress σ at frequency ν as a function of time *t*:

$$\sigma(t) = \sigma_0 \sin(2\pi \nu t) \quad . \qquad 2.2$$

This results in strain (ε) behavior described by the following expression:

$$\varepsilon(t) = \varepsilon_0 \sin(2\pi \nu t - \delta) \quad . \qquad 2.3$$

Here δ is a measure of the lag between the solid-like (elastic) and liquid-like (viscous flow) responses of the material. Data are typically reported in the form of the complex modulus E^*:

$$E^* = E' + iE'' \quad , \qquad 2.4$$

where i is equal to $(-1)^{1/2}$; E' is the storage modulus, E'' is the loss modulus, and

$$\tan\delta = \frac{E''}{E'} \quad . \qquad 2.5$$

The storage modulus represents the solid-like or elastic response of the material, while the loss modulus represents the liquid-like or viscous flow component.

2.2.3 Elongation at Break

Values for the elongation at break ε_b are averages obtained from the MatWeb Online Materials Database (www.matweb.com). Averages were used where a range of values was reported.

2.3 Sliding Wear and Viscoelastic Recovery

Tribology, as defined in Chapter 1, is concerned with the contacts between moving interfaces. The contacts can arise from a variety of geometries (flat surfaces, pin-on-flat surface, etc.); but here I consider the case where one interface, an indenter, is used to measure the resistance to deformation and wear of the other.

Repeatedly,[51-53] I have found micro-scratch testing by a diamond indenter to be a useful technique for evaluating scratch and wear resistance of materials. In fact, scratch deformation is critical in evaluating performance of plastics for different applications. Concerns range from simply degrading the aesthetics of a part to introducing sites for stress concentration and crack propagation. Scratching occurs often in transport even before a part arrives at the location where it will be used. For all these reasons, scratch testing is a relevant analytical technique. A simple scratch test consists of two passes of the indenter over a specified length. The first pass is conducted under the desired load for scratching; during this scan the instantaneous penetration depth R_p is measured. I mentioned earlier (in Chapter 1) that the viscoelasticity of polymers is a complication, but it can also be an advantage: namely that healing of the material can take place. The bottom of the scratch groove, left even for a brief time, goes up. During a second scan under low load, then, the residual depth R_h is measured at a depth typically much shallower than that of R_p. Typically, low values of R_p are associated with high hardness, while from the end-user's standpoint, the most important feature is R_h, the final depth of the observed scratch. Importantly, although the results of scratch testing may indicate hardness, there are fundamental differences between hardness testing and scratch testing. Scratch testing involves analysis over a trajectory while hardness is determined from indentation at a single point.

Sequential, multiple scratching of the same groove simulates sliding wear of the specimen surface [54]. Scratch resistance and sliding wear can be determined under a constant or progressive load. Although the former mode requires more experimentation, the results are more comprehensive. A question posed earlier in [55] was whether higher applied loads during sliding wear tests cause more and lasting damage and thus lower recovery than do low forces. The question was answered by determining the viscoelastic recovery for the various polymers listed in Table 2.1 and plotting the results as function of the applied load. The results are shown in Figure 2.1.

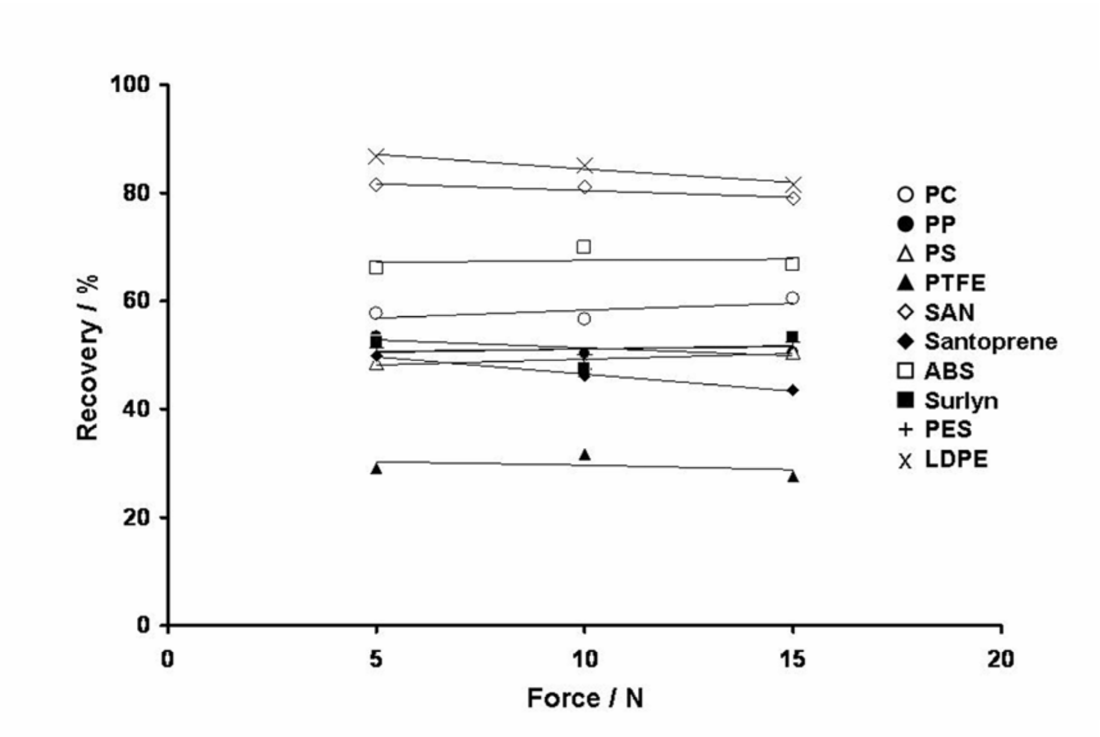


FIGURE 2.1. Viscoelastic recovery *f* in sliding wear (after 15 scratch tests) calculated from Eq. (1) as a function of the applied force *F* (in Newtons) for representatives of different classes of polymers. *Reprinted with permission from the Journal of Materials Research* [55] *and the Materials Research Society. Eq. (1) corresponds to Eq. 2.1 in the present document.*

From Figure 2.1 we see that in the range 5 to 15 N, the effect of the force applied on recovery is negligible. Of course, it is still true that higher forces result in higher values of R_p and R_h. What we observe then is similar to the Le Chatelier-Brown principle: the more we perturb the system, the more it resists the alteration. The viscoelastic recovery is therefore largely independent of the imposed experimental regime. This is the case for all polymers shown, even though their compositions are varied.

What, however, dictates the *amount* of recovery for each type of polymer? The materials science and engineering triangle [35] comes to mind. It tells us that the macroscopic properties of a material are determined by the microscopic structure and interactions. Therefore, we can conclude qualitatively that viscous flow in polymers is dependent on the amount of free space available for polymer chain rearrangements. How do we define that free space?

2.4 Viscoelastic Recovery and Free Volume

Let us return to the subject of viscoelasticity and the time-dependence of polymer properties. The phenomenon of creep [12,13,56-59] is a well-known instance where mechanical properties of polymers change with time. Because of such issues, dependable methods have been developed [12,13,57,58,60-63] to predict long-term service performance from short-term tests. As I have explained in an earlier work [55], a main component of these methods is the concept of free volume v^f. This is essentially the sum total of all the unoccupied space in a given specimen. Based on the time-temperature correspondence of polymer properties [64], we know that one can observe at higher temperatures (higher v^f) property changes that would take years or decades to occur if at lower temperatures (lower v^f). The free volume is defined [65] as:

$$v^f = v - v^* \qquad 2.6$$

where volumes are usually in $cm^3 \cdot g^{-1}$, v is the total specific volume, and v^* is the incompressible (hard core) volume. One can imagine that free volume would be "squeezed out" of a real material by cooling it down to 0 K and also applying an infinitely high pressure. Fundamental to the use of Eq. 2.6 is an equation of state of the form $v = v(T,P)$, where T is the thermodynamic pressure and P is pressure. Others [57,58,61-63] have shown for a variety of PBMs with different types of phases that one can obtain reliable predictions for decades of years by using in particular the Hartmann equation of state [66],

$$\tilde{P}\tilde{v}^5 = \tilde{T}^{3/2} - \ln\tilde{v} \quad . \qquad 2.7$$

The reduced parameters are defined as follows:

$$\tilde{v} = v/v^*; \;\; \tilde{T} = T/T^*; \;\; \tilde{P} = P/P^* \quad . \qquad 2.8$$

The use of hard-core or reducing parameters (v^*, T^*, P^*) improves comparability of different materials [65,66]. The concept of reduced variables goes back all the way to 1870 or so in the work of Johannes D. van der Waals. Litt [67] 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 $\tilde{v}$.[66] Hartmann and Haque explained and demonstrated the validity of Eq. 2.7 for amorphous polymers above and below the glass transition temperature. Thus, we can apply Eq. 2.7 even to polymers such as PS, PC, and PES which at room temperature are below the glass transition. The main concern then in correctly determining v^* from the Hartmann equation of state is to consider the thermal history for glassy polymers.

Zoller and Walsh [68] report a sizeable list of $v(T,P)$ data. Applying Eq. 2.7 to that data, v^*, T^*, and P^* for a subset of my materials were obtained. Using then Eq. 2.6, values for the free volume were determined.

For the select group of my polymers for which data were available, the percentage recovery is plotted in Figure 2.2 as a function of the free volume. Based on the earlier results of Figure 2.1, values of the percentage recovery in Figure 2.2 are averages (error is smaller than or equal to 3.2 % for all materials in Table 2.1) of those in the former. I hypothesized that a higher free volume would result in greater viscoelastic recovery in sliding wear. In agreement with that expectation, we see that higher free volume correlates with more recovery. Moreover, the values increase linearly, with the exception of polystyrene. Although the free volume was calculated based on tabulated P-V-T data, we can reasonably expect that experimental results for the actual specimens would be similar to the results calculated from the tabulated values. Thus we expect that PP fits the linear trend, but PS is clearly an outlier. What could be the reason for the sole exclusion of PS? A 2005 publication on strain hardening of polymers [69] seems relevant here.

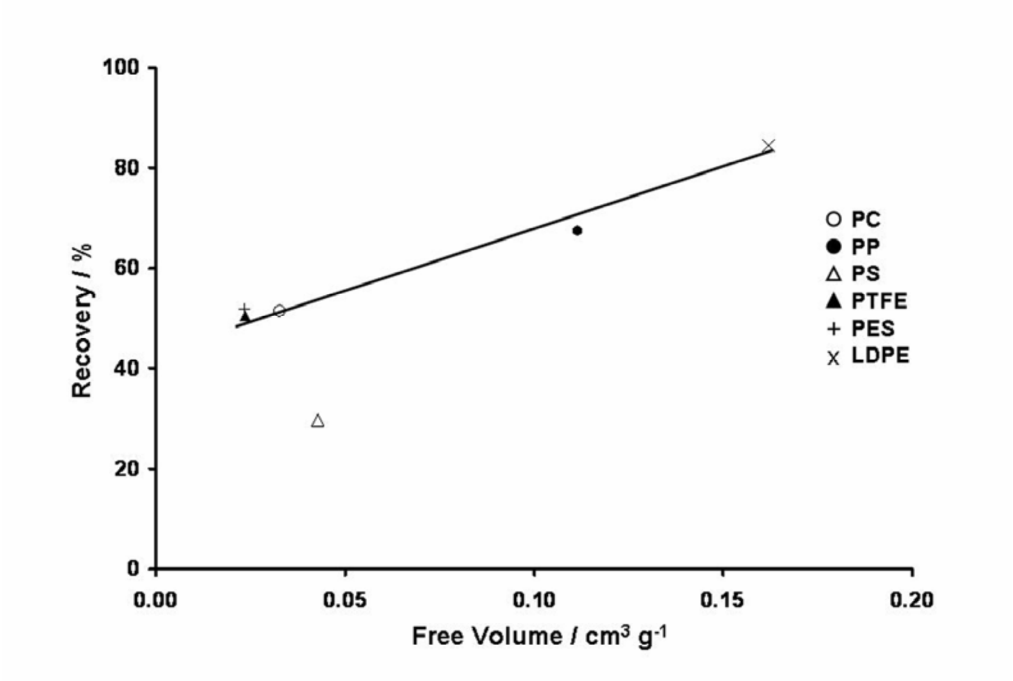


FIGURE 2.2. Percentage recovery determined in sliding wear tests for representatives of different classes of polymers. The average viscoelastic recovery f is plotted as a function of the free volume v^f of the corresponding material. The correlation line is for a linear least squares regression of all points excluding that for PS (R^2 *value* = 0.978). *Reprinted with permission from the Journal of Materials Research* [55] *and the Materials Research Society. Values for the free volume were calculated using Eq. 2.6.*

2.5 Strain Hardening and Brittleness

The discovery of strain hardening in sliding wear was first reported in 2004.[48] Three polymers were studied, and it was shown that after about 10 passes of the indenter, the residual depth remained constant. In other words, further scratching did not cause any more wear of the material. Since that first report, other materials have been investigated at varying forces and sliding speeds [69,70]. Strain hardening was observed for all polymers except polystyrene, which also in this case is seen as an outlier here in Figure 2.3. The different ordinate scales for PES, Santoprene, PC, and PS in Figure 2.3 immediately suggest their different properties, in particular that the softer and rubbery Santoprene is penetrated most deeply while PS and PC are not as easily scratched. This also confirms that one of the original objectives, namely covering distinct categories of polymeric materials with significantly different properties seems to have been achieved.

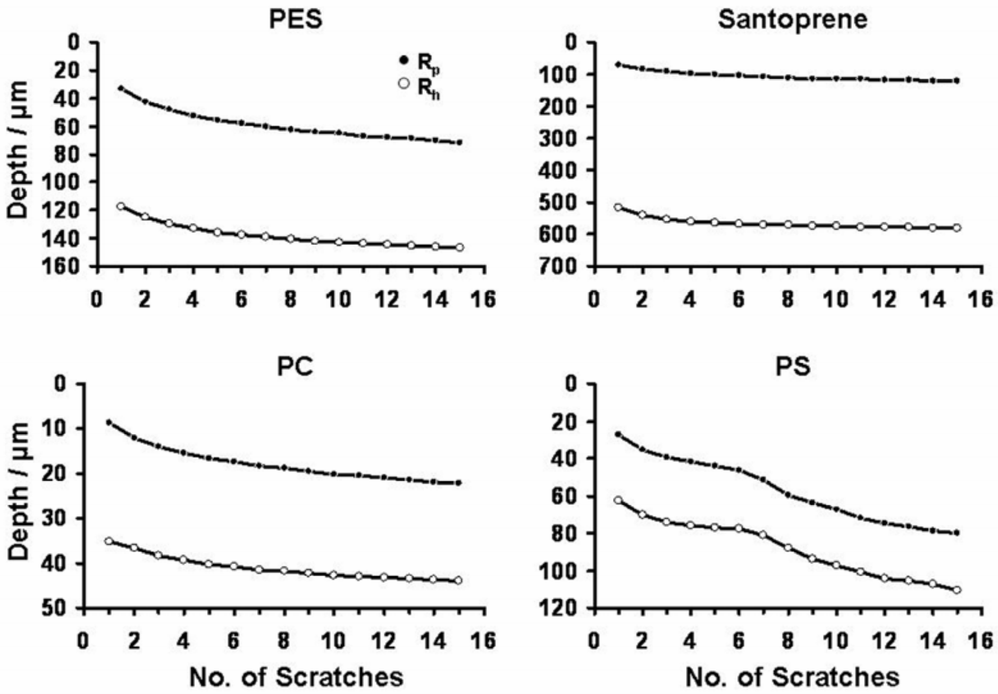


FIGURE 2.3. Penetration depth R_p and residual depth R_h values as a function of the number of scratching tests performed in sliding wear determination. Strain hardening observed for all materials, also for different force levels, except for polystyrene. Plots are for PES at 22.5 N, Santoprene at 15 N, PC at 5 N, and PS at 15 N. *Reprinted with permission from the Journal of Materials Research* [55] *and the Materials Research Society.*

What can explain the data on polystyrene in Figures 2.2 and 2.3? Karger-Kocsis and coworkers [71] studied polyamide 12 blends with styrene-containing copolymers. The authors appreciated the easy melt processability of PS. However, they found that maleation of the styrene-containing copolymers was necessary to obtain good mechanical performance and overcome innate brittleness of PS. A qualitative answer then is that brittleness—for which PS is infamous—explains the behavior of polystyrene.

Then there is a catch: how is brittleness quantified? A definition was outlined in 2006 [55], and the logic is now explained here. We return to viscoelasticity, the main feature of PBMs. The usual method to characterize viscoelasticity of polymers is dynamic mechanical analysis [49,50], of which the basics were already discussed in Section 2.2.2. Simply, we are applying an oscillating force to a specimen and analyzing the material's response. The stiffness of the material and its ability to recover from deformation correspond to the measured value of the storage modulus E'. This component is that which is in phase with the applied oscillating force. The tendency of the material to flow—its viscosity—is determined by the phase lag and is characterized by the loss modulus E''. Physically what is happening during a temperature scan under an oscillating force is that the free volume and dynamics of polymer chain relaxation are changing [49]. A thorough and detailed discussion of effects of free volume on properties of polymeric materials has been provided by Paul Flory and his collaborators [65].

Considering this type of results, what brings us closer to understanding brittleness? Obviously, it is not the extent of liquid-like behavior (E'') that produces brittleness. E', however, is a candidate. The importance of the storage modulus lies in the fact that it represents resistance of the material to deformation under repetitive loading. This is in contrast to other elastic modulae that also represent resistance to deformation but in one-time loading. One would expect a material with a high storage modulus to be not brittle. This alone, however, seems insufficient to measure brittleness.

Reasoning further that the apparent opposite of brittleness is ductility. This concept is not particularly useful, however, since we can find in use more than one measure of ductility. Another idea comes to mind: toughness, which is often also contrary to brittleness. Toughness is frequently defined as the area (by integration) under a stress-versus-strain curve obtained by quasi-static tensile testing. The value obtained by this method corresponds to the energy absorbed at break (failure). We can see from this that the elongation at break ε_b, in addition to the resistance to deformation (E'), is important to brittleness. Clearly, a material with a high elongation at break will not be brittle, thus an inverse relationship is proposed. Following this reasoning, I put forth with my coauthors [55] this definition of brittleness (B):

$$B = 1/(\varepsilon_b E') \quad . \tag{2.9}$$

The definition assumes a value of E' corresponding to 25 °C from testing at 1.0 Hz and a value of ε_b taken also at that temperature.

2.6 Calculating Brittleness

The next logical question: does Eq. 2.9 adequately describe brittleness? B was calculated for the same set of materials shown in Figure 2.1 and then plotted versus the viscoelastic recovery. This is shown in Figure 2.4, where the line corresponds to the equation

$$B = b_1 e^{-f/b_2} \tag{2.10}$$

On the y-axis, values are actually $10^{10}B$ (see also Table 2.2). From a least squares fit, $b_1 = 422.5$ and $b_2 = 7.644$. With the correlation coefficient $R^2 = 0.9941$, we recognize that Eq. 2.10 is obeyed with high accuracy for all the materials shown, thus b_1 and b_2 can be considered as "universal" constants. It follows that b_1 determines the magnitude of B; it therefore depends on the units of E'. b_2 can be said [55] to represent the coupling strength between brittleness and recovery; a higher value of b_2 would diminish the effect of f on B. In other words, the value of b_2 indicates (inversely) to what extent brittleness is determined by the recovery.

In general terms, Figure 2.4 shows that high recovery in sliding wear corresponds to low brittleness and vice versa. In contrast to Figures 2.2 and 2.3, here polystyrene has been 'brought into the fold'. Moreover, this outcome coincides with our intuition about brittleness. Another glance at Figure 2.4 shows a steep drop from polystyrene to all other materials, suggestive of a threshold B value. Therefore, non-brittle behavior would correspond to that in Figure 2.2, where sliding wear recovery is a linear function of the free volume. The extremely high B value for PS also explains its failure to exhibit strain hardening under sliding wear.

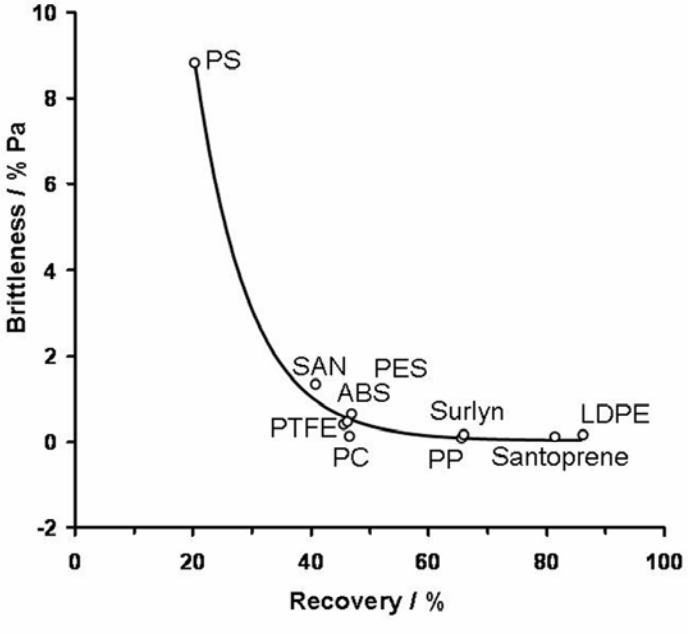


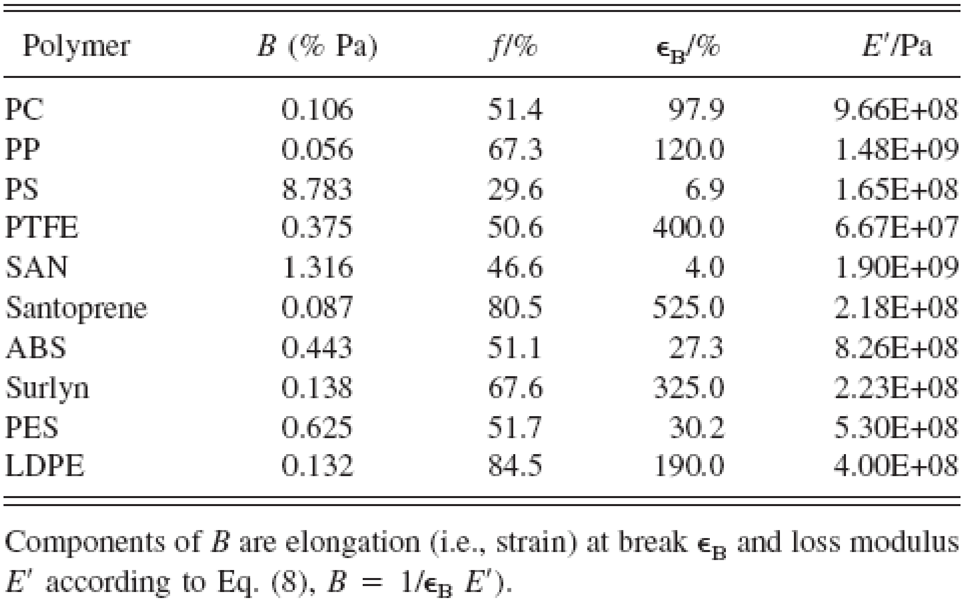
FIGURE 2.4 Brittleness B, defined by Eq. (8), as a function of the viscoelastic recovery f for representatives of several classes of polymers. Circles represent experimental points. The units are $10^{10}B/(\%\cdot\text{Pa})$. The continuous line has been calculated by using Eq. (9). The error in recovery values for all materials shown is less than or equal to 3.2%. *Reprinted with permission from the Journal of Materials Research* [55] *and the Materials Research Society. Eqs. (8) and (9) correspond to Eqs. 2.9 and 2.10, respectively, in the present document.*

2.7 Discussion

2.7.1 Brittle Polymers

How do polymers such as poly(phenylene sulfide) (PPS) and poly(ether ether ketone) (PEEK) fit into this definition of brittleness? Sufficient data on PPS were not found, but for PEEK, the values $\varepsilon_b = 50$ % and $E' = 3.634 \cdot 10^9$ Pa have been reported (see [55]). This gives 10^{10}B/(% Pa) = 0.055, a value similar to that for PP shown in Table 2.2. Consequently, despite that the normally crystalline polymers PPS and PEEK are sometimes called brittle, the value of *B* by Eq. 2.9 for PEEK indicates that it is not brittle. This outcome finds validity in the wide use of PPS and PEEK as matrices for high-performance composites. In addition, after calculation of the free volume for PEEK,[55] that value (0.115 cm^3g^{-1}) too was in close agreement with the one for PP, further confirming the validity of the model. The predicted viscoelastic recovery for PEEK is therefore $f \approx 70\%$.

TABLE 2.2. Values of brittleness *B* expressed as $10^{10}B/(\%\cdot Pa)$ for representatives of several classes of polymers compared with the viscoelastic recovery *f*. *Reprinted with permission from the Journal of Materials Research* [55] *and the Materials Research Society. Eq. (8) below corresponds to Eq. 2.9 in the present document, while similarly* ϵ_B *is equivalent to* ε_b.



Polymer	*B* (% Pa)	*f*/%	ϵ_B/%	*E′*/Pa
PC	0.106	51.4	97.9	9.66E+08
PP	0.056	67.3	120.0	1.48E+09
PS	8.783	29.6	6.9	1.65E+08
PTFE	0.375	50.6	400.0	6.67E+07
SAN	1.316	46.6	4.0	1.90E+09
Santoprene	0.087	80.5	525.0	2.18E+08
ABS	0.443	51.1	27.3	8.26E+08
Surlyn	0.138	67.6	325.0	2.23E+08
PES	0.625	51.7	30.2	5.30E+08
LDPE	0.132	84.5	190.0	4.00E+08

Components of *B* are elongation (i.e., strain) at break ϵ_B and loss modulus *E′* according to Eq. (8), $B = 1/\epsilon_B E'$).

2.7.2 Aging of Polymers

It is well known and also reported in the literature [72,73] that polymers grow brittle with age. With respect to Eq. 2.9, what happens to ε_b and E' with aging? Simple reasoning tells us that if both decrease, then brittleness increases; or if E' increases then ε_b must decrease faster. Data for both properties on neat polymers is difficult to find, as generally one or the other property is reported and often for a particular blend or composite. One of those is Hypalon®, a chlorosulfonated polyethylene, and another is a tri-layered Hypalon with Neoprene®.[74] For both of these materials, it is reported that E' increases while ε_b decreases with aging.[74] Specifically, after aging 88 days E' increased an estimated 16% for Hypalon and 24% for the tri-layered Hypalon. During the same time period, the average decrease in ε_b for Hypalon samples was 20% and for the tri-layered Hypalon 45%. Therefore elongation at break decreased faster than storage modulus increased, validating the measure of brittleness defined by Eq. 2.9. This also agrees with reports such as [72] that aging produces embrittlement.

Schwarz and coworkers have studied aging of neat polypropylene and report data on the storage modulus and on the strain at yield.[75] If we make the reasonable assumption that elongation (i.e. strain) at break behaves in the same way as strain at yield, then we find from their work that for PP both E' and ε_b decrease with aging. Clearly, the decreased values would result in a higher value for B. Thus, a second report from the literature indicates that Eq. 2.9 can be used even to describe the brittleness that occurs with aging.

2.8 Summary

Mayer notes in his book on fiber-containing PBMs [76] that “the designer needs to be aware of what is and is not possible with today’s materials and production techniques.” With the connections defined above, and a definition of brittleness appropriate for polymers, one expects this definition will be useful for others as a design criterion.

CHAPTER 3

PHASE 2 – PROOF OF PRINCIPLE

3.1 Introduction

With the connections established in Chapter 1 of this work, we have seen progress toward the ability to predict one type of property based on another. A general definition of brittleness the definition (Eq. 2.9) was applicable to a variety of thermoplastics and thermoplastic elastomers. In proof of the principle defined, additional polymers are now considered to confirm the correlation between brittleness B and viscoelastic recovery f in sliding wear.

3.2 Materials

Materials reported in this chapter include those listed in Chapter 2, Table 2.1 plus three additional thermoplastic polymers (Set 2): poly(methylmethacrylate) (PMMA) from RTP Company; polyphenylsulfone (PPSU) from Solvay Advanced Polymers, L.L.C.; and polyvinylidene fluoride (PVDF) from Solvay Solexis, Inc.. PMMA, PPSU, and PVDF specimens were prepared by compression molding from standard unfilled injection-molding grade pellets. These three polymers were selected to represent different rigidity schemes and structures: PVDF is a relatively soft semicrystalline fluoropolymer, PMMA is semicrystalline and hard (also known as Plexiglas in the Americas and as Perspex in Europe), while PPSU is amorphous, hard, and very heat and chemicals resistant. All are common widely used engineering thermoplastics.

3.3 Experimental Procedures

3.3.1 Sliding Wear

Sliding wear tests were conducted according to the same procedure described in Chapter

2, Section 2.2.1. Each test consisted of 15 scratches; values for R_p and R_h were recorded and the recovery f calculated from Eq. 2.1. Based on the fact that f is independent of the load (as described in Figure 2.1 and the related text), the values of f reported for PMMA, PPSU, and PVDF are from sliding wear under an applied load of 5.0 N.

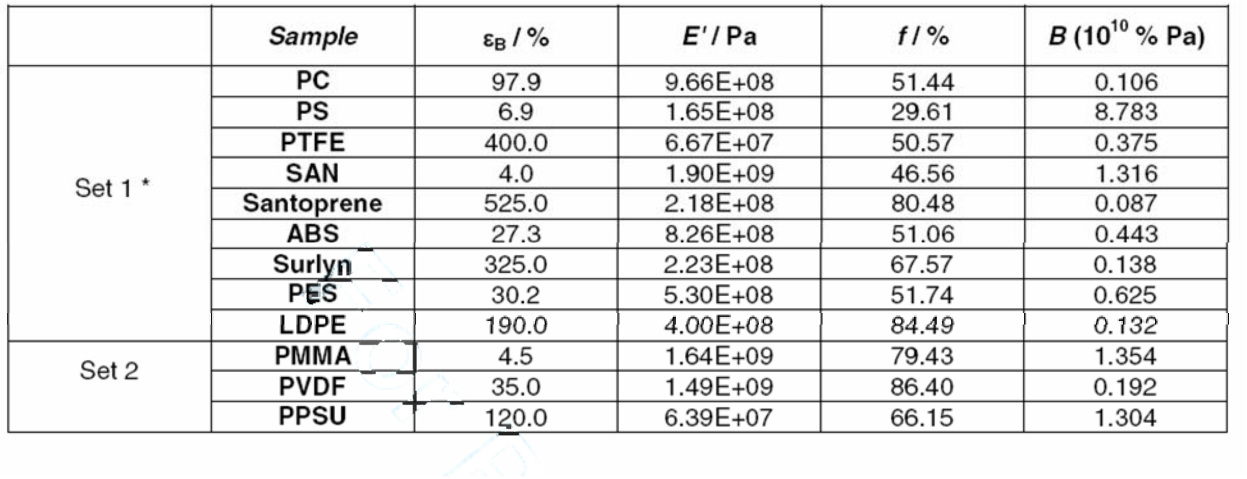
3.3.2 Dynamic Mechanical Analysis

DMA was performed exactly as described in Section 2.2.2. Reported values of the storage modulus E' correspond to the temperature 25 °C.

3.3.3 Elongation at Break

As in Section 2.2.3, values for the elongation at break ε_b for PMMA, PPSU, and PVDF were obtained from the MatWeb Online Materials Database (www.matweb.com), using averages where a range of values was reported.

TABLE 3.1. Tabulated values for elongation at break ε_b, storage modulus E', viscoelastic recovery f, and brittleness B. *Reprinted with permission from Polymer Engineering and Science and Wiley Publishers* [77]*. * Set 1 data appear also in Chapter 2 of the present document.*



	Sample	ε_B / %	E' / Pa	f / %	B (10^{10} % Pa)
Set 1 *	**PC**	97.9	9.66E+08	51.44	0.106
	PS	6.9	1.65E+08	29.61	8.783
	PTFE	400.0	6.67E+07	50.57	0.375
	SAN	4.0	1.90E+09	46.56	1.316
	Santoprene	525.0	2.18E+08	80.48	0.087
	ABS	27.3	8.26E+08	51.06	0.443
	Surlyn	325.0	2.23E+08	67.57	0.138
	PES	30.2	5.30E+08	51.74	0.625
	LDPE	190.0	4.00E+08	84.49	0.132
Set 2	**PMMA**	4.5	1.64E+09	79.43	1.354
	PVDF	35.0	1.49E+09	86.40	0.192
	PPSU	120.0	6.39E+07	66.15	1.304

3.3.4 Calculation of Brittleness

Brittleness of PMMA, PPSU, and PVDF was calculated using Eq. 2.9. Units for ε_b and E' were % and Pa, respectively, as before. The values are given in Table 3.1.

3.4 Results and Discussion

Recall the stated objective that we need PBMs with better wear-resistance, and this requires improved understanding. As a consequence, I pursued a relationship between tribological (e.g. wear) and mechanical properties based on the physical structure of the tested materials. I have demonstrated already that viscoelastic recovery increases with the free volume. Further, brittleness has been defined in a way that correlates with the commonly understood meaning of the word. Now we see in Figure 3.1 the dependence of *f* on brittleness.

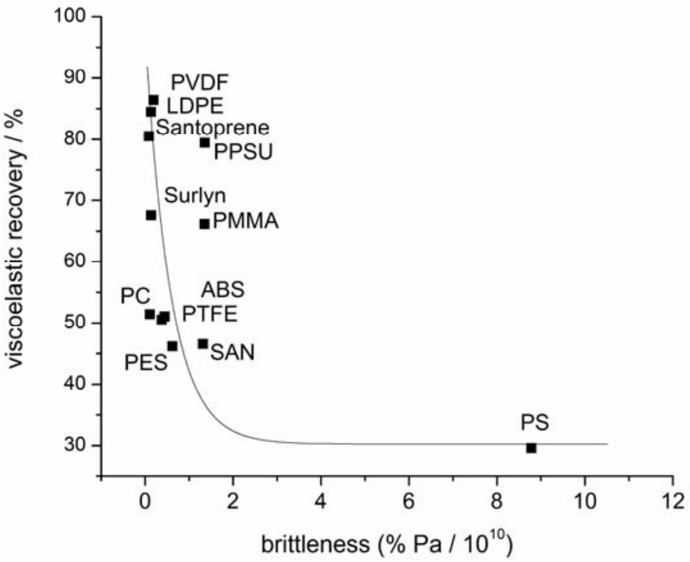


FIGURE 3.1 Percentage of viscoelastic recovery *f* in sliding wear obtained from Eq. (1) as a function of brittleness *B* calculated from Eq. (2). *Reprinted with permission from Polymer Engineering and Science and Wiley Publishers* [77]*. Eqs. (1) and (2) correspond to Eqs. 2.1 and 2.9, respectively, in this document.*

The best fit line is in the form of exponential decay while the scatter of points is expected given that the ε_b values are averages taken from a database and not measured directly. PS has high brittleness and relatively little viscoelastic recovery. Other materials which have lower brittleness also have higher recovery and therefore lower wear. PMMA and PPSU have values of B slightly higher than the other materials, but they clearly still fall significantly below the value for polystyrene. Moreover we know that these materials are widely used in high-performance

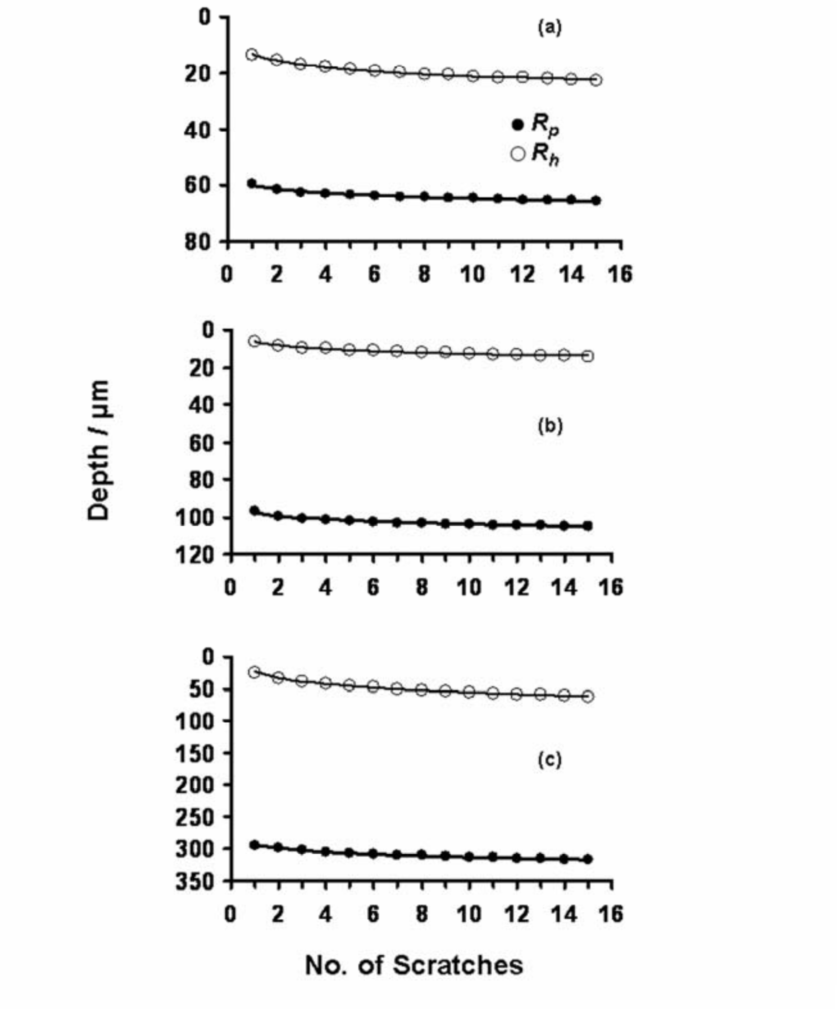


FIGURE 3.2. Sliding wear profiles for (a) PMMA, (b) PVDF, and (c) PPSU. Penetration depth R_p and resididual depth R_h are plotted versus the number of scratches under a 5.0 N applied load. *Reprinted with permission from Polymer Engineering and Science and Wiley Publishers* [77].

applications. Furthermore, until now PS has been the only polymer identified that does not exhibit strain hardening in sliding wear. This remains the situation as Figure 3.2 indicates that PMMA, PPSU, and PVDF all show strain hardening. For each of these three materials, we observe the characteristic plateau of both the penetration and residual depths, even though the rate at which the strain hardening occurs differs slightly among the polymers.

Therefore the benefits of the model of brittleness that I have defined are several. It distinguishes non-brittle materials as those that show strain hardening in sliding wear. Moreover, there is a correlation between brittleness and the viscoelastic recovery that occurs during sliding wear. Furthermore, this definition of brittleness applies to a broad range of materials.

Quinn and Quinn proposed in 1997 a new index of brittleness based on the hardness, Young's modulus, and fracture toughness for ceramics.[47] The use of the Young's modulus is better suited to compare ceramics and metals while the incorporation of storage modulus makes possible inclusion of viscoelastic materials, allowing wider use of the new definition. The use of hardness to define brittleness assumes the value corresponds to deformation energy rather than fracture energy during indentation. Given the load dependency of hardness, Quinn and Quinn chose to use plateau Vickers hardness values to minimize the influence of the fracture energy component. The third term of the brittleness index defined by Quinn and Quinn is fracture toughness, which in contrast to hardness should correspond to the fracture energy. In other words, this parameter is distinctly linked to a brittle mode of failure. This is not a problem for ceramics, but determining the corresponding plane-strain-fracture toughness for polymers requires that the testing be done under conditions to give brittle failure.[78] These conditions are not always (and easily) obtained, particularly since small sample sizes common in laboratory testing may inhibit obtaining the necessary strain and result in ductile rather than brittle fracture.

Consequently, the brittleness index defined by Quinn and Quinn, while applicable as they have described for ceramics (within certain limitations), is not ideal to describe viscoelastic polymers. We have already noted Matsuoka's [40] observation that the strength of polymers can be unrelated to the Young's modulus. Further, based on the discussion by Quinn and Quinn, we should not take hardness values for polymers without first identifying the load dependence. This along with the unadvisable assumption that reported values of fracture toughness necessarily correspond to a brittle mode of failure for plastics preclude the immediate use of their brittleness index for PBMs. The definition of brittleness I proposed above accounts for stiffness and fracture based on techniques relevant for viscoelastic materials.

CHAPTER 4

PHASE 3 – BRITTLENESS OF MATERIALS

4.1 Introduction

Now with a working scale of brittleness, we are poised to look at a greater variety of materials. Because the storage modulus measured by dynamic mechanical analysis and the elongation at break from a tensile force will react to changes in polymer composition and structure, one can potentially observe the effects of fillers, modifiers, etc. on the behavior of the polymer matrix. Furthermore, it would be interesting to see the brittleness values for other materials such as metals. Experiments along these lines were pursued and the results reported in the remainder of this chapter.

4.2 Materials

Materials reported in this chapter include those mentioned previously plus new materials listed in Table 4.1. The materials were selected as they have different compositions and structures. Hytrel is a block copolymer thermoplastic elastomer composed of rigid poly(butylene-terephthalate) (PBT) and flexible poly(tetramethylene oxide) (PTMO). The average size of added aluminum flakes was 125 nm. Polycaprolactone is a biodegradable polyester; the non-branching chains of PCL result here in a semi-crystalline material. Silica added to PCL had an average particle size of 4.1 μm. UHMWPE differs from other polymers because of the unusually high molecular weight of its polymer chains, which make it viscous even at elevated temperatures and thus difficult to melt and mold. The 2 % by weight of white graphite added appears as 5 to 15 μm bundles of platelets (shown later in section 4.4). Here the term white graphite refers to an undisclosed experimental material provided by a company with the agreement its identity shall not be released. The material is like graphite only in that it can be used as a solid lubricant. The material called CBDO here is actually a co-polymer (specifically a co-polyterephthalate) of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) as described in a paper by Beall et al [79].

Polymer and polymer composite specimens were prepared by compression molding in a Carver hot press. 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. Steel and aluminum alloys were machined into the appropriate specimen shapes.

TABLE 4.1 List of materials (Set 3) including abbreviations and manufacturer or description of composition.

Material	Abbreviation	Manufacturer/Description
Hytrel®	Hy	E.I. du Pont de Nemours
Hytrel + aluminum	HyAl	(10 % aluminum nanopowder)
Polycaprolactone	PCL	Solvay
Polycaprolactone + silica	PCL-SIL	(10 % silica micropowder)
Ultrahigh molecular weight polyethylene (UHMWPE)	UH	Ticona
UHMWPE + white graphite	UHWG	(2 % white graphite micropowder)
Copolyester	CBDO	Proprietary
Steel	Steel	(314 stainless steel)
Aluminum	Al	(6061 alloy)

4.3 Experimental Procedures

4.3.1 Sliding Wear

For all materials listed in Table 4.2.1, sliding wear tests were conducted at 5.0, 10.0, and 15.0 N (3 runs at each force) at 5 mm/min sliding speed over a 5 mm groove. The penetration and residual depth were determined by averaging the values between 0.5 and 4.5 mm along the scratch groove. The percentage recovery was calculated according to Eq. 2.1 given in Chapter 2. The results reported are averages from the several runs at 5, 10, and 15 N. The average error in recovery for materials in Set 3 was ± 2.3%, while the highest single value for one material at a single force was ± 7.5%.

4.3.2 Dynamic Mechanical Analysis

Specimens were tested similarly to those described earlier using the three-point-bending apparatus at frequency 1.0 Hz. Tests consisted of a temperature scan from -15 °C to 60 °C at 5 °C/min. The static and dynamic loads were adjusted to maintain the amplitude of deflection at 5 μm at the start of each run. The static force was always 10 % higher than the dynamic force. As before, reported values of E' are for the temperature 25 °C. PMMA and PPSU (of Set 2) were also re-run under these conditions. The average error was 19% of the reported E' values.

4.3.3 Tensile Testing

The elongation at break was determined by tensile testing on an 810 Material Test System (MTS Systems Corporation). Dog-bone shaped specimens (see Figure 4.1) 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). For both polymer and metal samples, necking occurred in the narrow section before appearance of a horizontal fracture at break. Figure 4.1 shows a dog-bone specimen of UH mounted in the test system at the start of testing. The testing speed was adjusted for different classes of materials: 1.27 mm/min for rigid samples (Steel, Al, CBDO); 50.8 mm/min for semi-rigid samples (UH, UHWG); 200 mm/min for flexible samples (PCL, PCL-SIL, Hy, HyAl). The elongation at break ε_b was calculated from the original gauge length l_0 and the length l at break as follows:

$$\varepsilon_b = \frac{l - l_0}{l_0} \times 100\% \qquad 4.1$$

Values reported are averages from 5 runs. The values obtained for neat polymers were in agreement with those in the online MatWeb database.

FIGURE 4.1. Dog-bone shaped specimen of UH mounted in the tensile testing Material Test System. The sample is shown at the start of the test before elongation.

4.3.4 Environmental Scanning Electron Microscopy

Micrographs of fractured sample surfaces were obtained using an FEI Quanta 200 environmental SEM (ESEM). We collected images using variable pressure (low vacuum) mode to reduce specimen charging. Specimens were not coated prior to examination. The electron beam accelerating voltage was 15 kV while the pressure used is indicated in the image databars.

The large field secondary electron detector was used for all of the images with an analytical working distance of 10 mm.

4.4 Results

The samples in Set 3 again come from different classes of materials and possess therefore a variety of chemical compositions and structures. In UHMWPE we have a long chain linear polymer with intrinsic low friction and composed of only hydrogen and carbon. PCL is a biodegradable polyester while Hytrel is a thermoplastic elastomer. For each of these polymers and their respective blends with either metal or ceramic powders, strain hardening is observed in the sliding wear profiles. See for instance several charts of the depth versus scratch number shown in Figure 4.2. Similarly CBDO also exhibits strain hardening. By contrast, there is little strain hardening in sliding wear for the metals, especially aluminum, under the same test conditions (see Figure 4.3). Although the curves for steel in Figure 4.3 have somewhat leveled by the 15th pass of the indenter, it appears that the depths are still increasing. Plastic deformation and the propagation of defects may prevent toughening of the scratch groove in crystalline metals such as stainless steel and aluminum. It has been demonstrated elsewhere that for sliding wear one mechanism of strain hardening in polymers is densification.[80] Of course the mechanism for work hardening in metals differs from that for polymers. It is possible for either work hardening or work softening to occur in metals from the strain induced by repetitive scratching [81,82]; what occurs is very dependent on composition and whether the metal is crystalline or amorphous. For amorphous metals, Rigney [82] reported a decrease in density accompanied by increased free volume leading overall to work softening. He suggests also that simple crystalline metals are more likely to work harden under sliding wear type conditions, but this is not universally true for all crystalline metals.[81] As stated in the experimental procedures, the percentage recovery was calculated from the sliding wear profiles for each material.

Looking more closely at the sliding wear profiles, we see that the addition of only 2 % by weight of white graphite powder to ultra-high molecular weight polyethylene has almost no effect on its properties. ESEM micrographs of UH, WG, and the composite UHWG are shown in Figure 4.4. We observe agglomerates of WG platelets and ridged particles of un-melted UH powder. A surface of the molded UH appears smooth and fairly homogeneous. In the composite, WG particles were very widely dispersed and difficult to find; an image in Figure 4.4 shows the

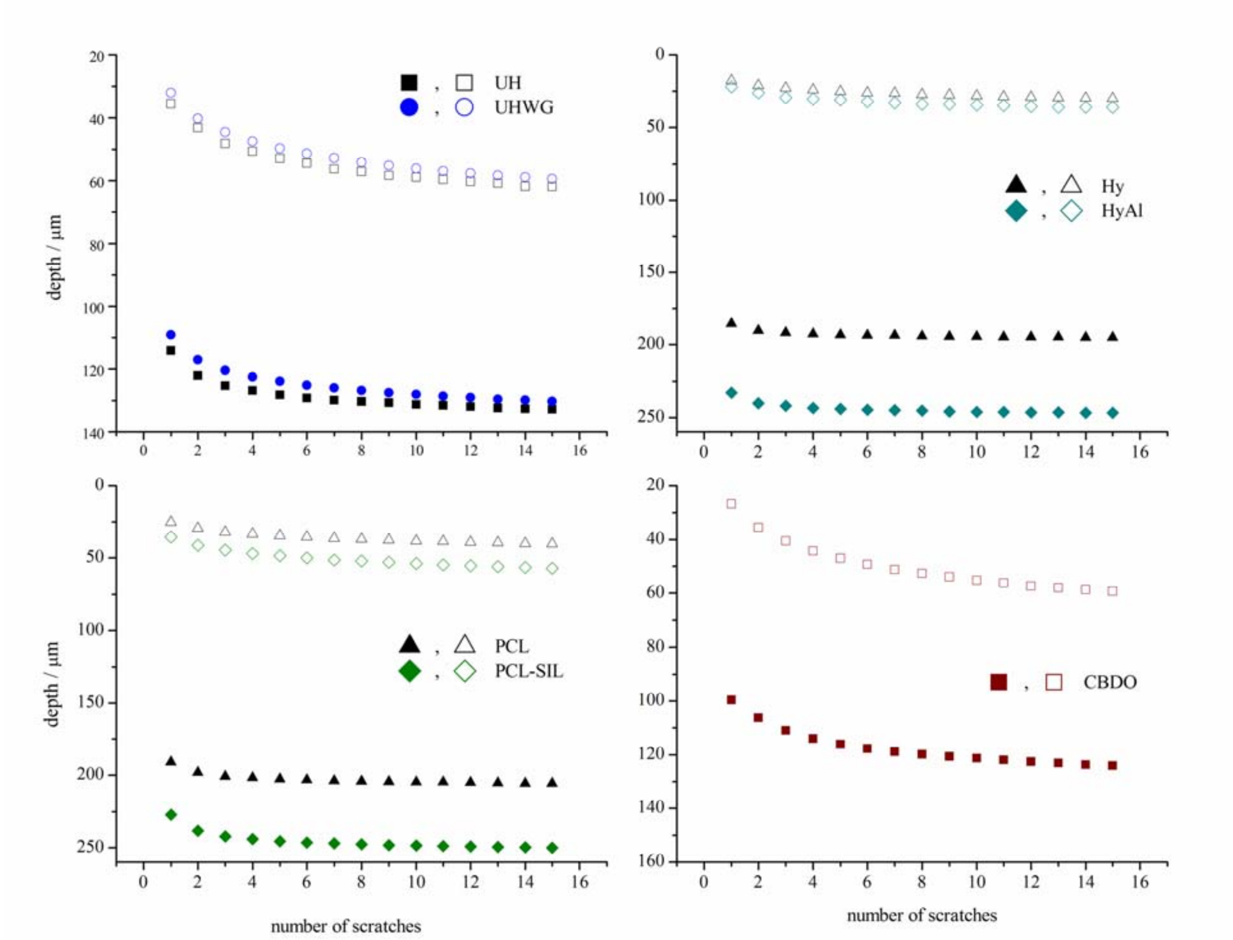


FIGURE 4.2. Sliding wear profiles of polymers and polymer composites in Set 3. Closed symbols are used for the penetration depth R_p and open symbols for the residual depth R_h. The applied for testing was 10.0 N.

platelets sitting in the polyethylene matrix with apparently little cohesion. While this situation would tend to weaken the neat UH, in this particular case extensive entanglements in the high molecular weight polymer likely reduce the overall effect of the added particles.

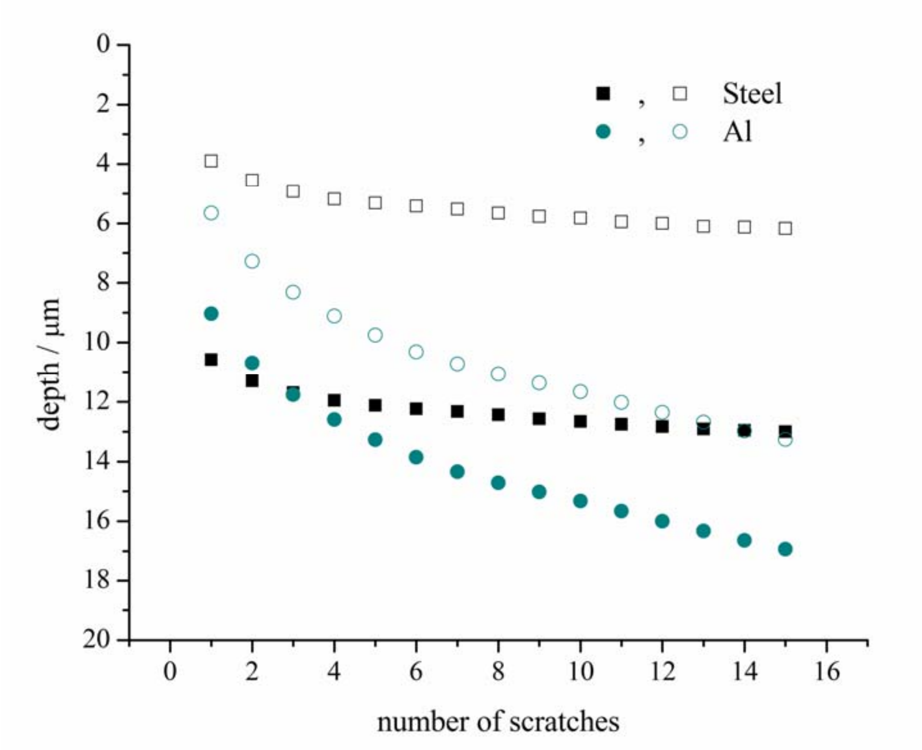


FIGURE 4.3. Sliding wear profiles of aluminum and steel specimens under a 10.0 N applied load. Closed symbols correspond to R_p and open symbols correspond to R_h.

For Hytrel and PCL we find that the addition of aluminum and silica powders, respectively, result in slightly larger changes in the sliding wear behavior (Figure 4.2). Both HyAl and PCL-SIL are penetrated more deeply than their respective homopolymers. This may occur because the integrity of polymer chain interactions is disrupted by the particles. Typically, there is an ideal filler concentration to reinforce a polymer’s properties; concentrations above or below that have a negative effect. Further, the ESEM images in Figure 4.5 provide evidence of poor adhesion of PCL to silica. Note especially in Figure 4.5(b) a particle of silica standing in the polymer matrix. We also note that strain hardening occurs very quickly—within the first 4 scratches—for PCL and Hy.

These results (of sliding wear recovery) along with values for the elongation at break and storage modulus are listed in Table 4.2. Clearly there are materials with varying extents of ductility and stiffness. Using Eq. 2.9, the definition of brittleness that I defined earlier, values of *B* were calculated with the results shown also in Table 4.2. The brittleness values of Set 3 are compared to those of Sets 1 and 2 in Figure 4.6. We observe for PBMs a range of low values of brittleness and again a large gap to the value for PS. Given the very large storage modulae of aluminum and steel, it is not surprising that their brittleness is quite low, with aluminum slightly more brittle than stainless steel.

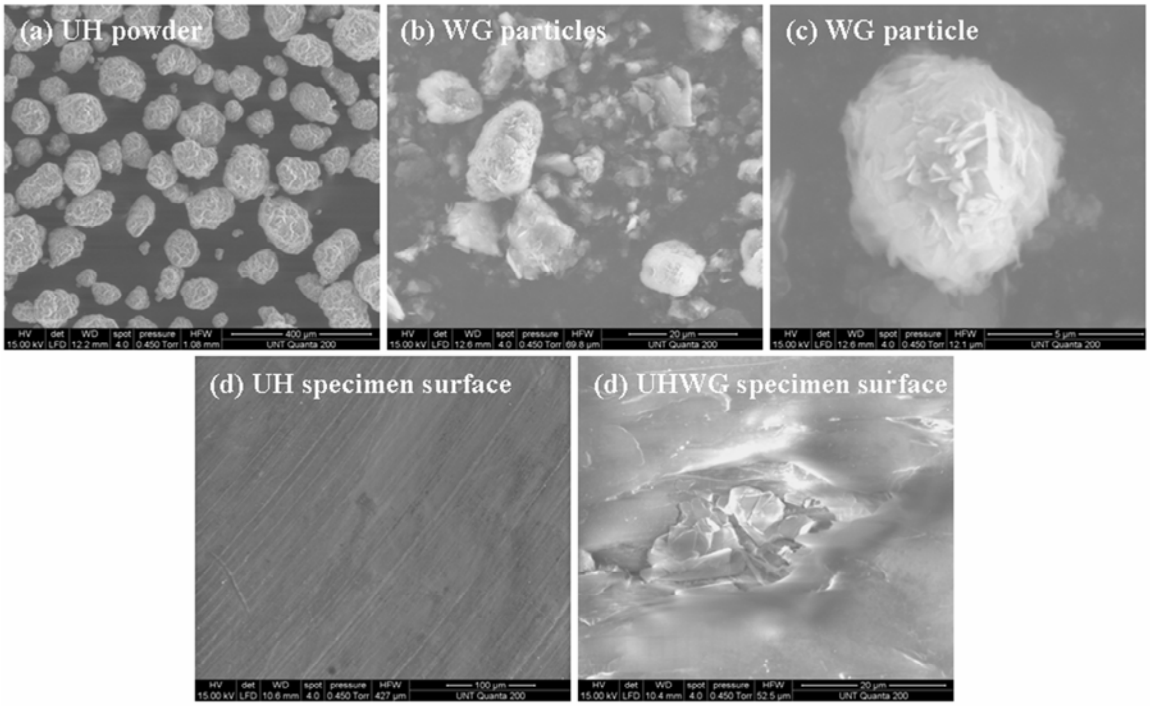


FIGURE 4.4. Micrograph images (ESEM) of the as-received UH powder and unmodified WG particles as well as of molded specimens of UH and the composite UHWG.

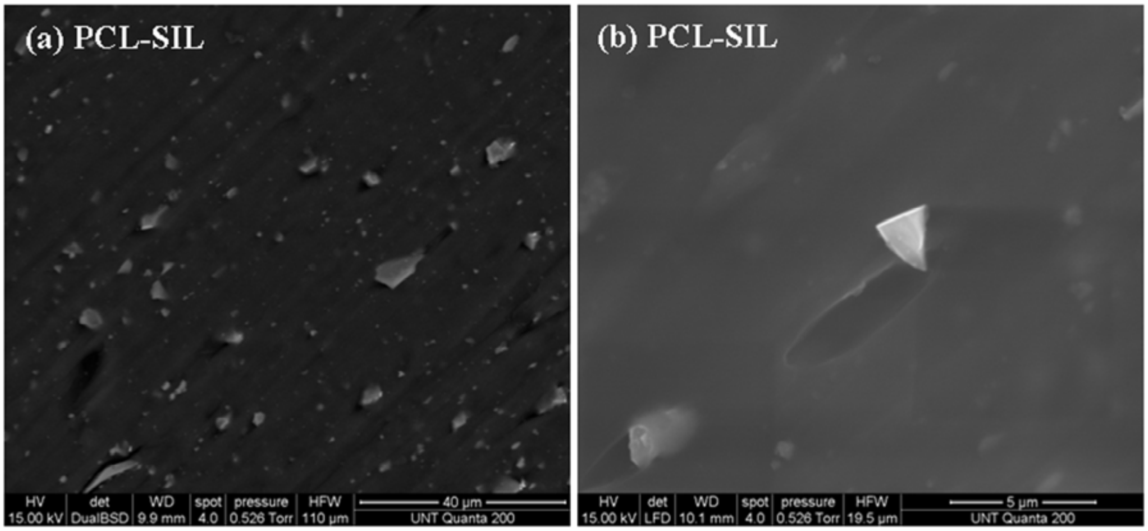


FIGURE 4.5. Micrograph images (ESEM) of different locations on a molded specimen of the composite PCL-SIL.

What about the connection of brittleness to recovery? Data for all three sets are plotted in Figure 4.7; and the data are fit by an exponentially decaying curve. We note that for metals the recovery in scratch testing is elastic in nature. This is further evident in that based on the exponential curve and the B values obtained for Steel and Al, one would expect higher recovery than what is observed. This difference corresponds to the viscous component that is present mainly in the case of polymeric materials.

Comparison of this wide range of material types is not dependent on all materials exhibiting the same type of fracture. For instance, 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. Another way of describing this is that above the transition there is sufficient free volume to give ductile fracture and below it a small free volume yields brittle fracture. The values E' and ε_b do not require that all materials be at a temperature within a defined region of a particular mode. Instead the two parameters measured at the same temperature permit comparison of different materials under similar environmental conditions.

4.5 Summary

We can conclude then the universality of the definition of brittleness for polymers laid out here and its usefulness in prediction. In the case of polymer composites, for instance, where ε_b and E' may respond differently and to varying extents, the B value provides a unified comparison of final performance to that of the unmodified matrix material. Thus we have the brittleness of Hy and HyAl nearly identical: although elongation decreased by addition of aluminum to Hytrel, the aluminum also increased the storage modulus of the material. On the other hand, there is a slightly larger gap between the B values of PCL and PCL-SIL. This difference is likely overstated, however, since it should be noted that artifacts of tensile testing may influence the outcome when the elongation is extremely large, as it is for PCL. Since some PCL specimens never fractured, the resulting average elongation is skewed. Therefore we can confidently believe that the storage modulus of PCL-SIL is higher than that of PCL, but we expect that under modified tensile testing conditions, we would find generally a lower value for the elongation at break of PCL with added silica.

Again reviewing the figures in this chapter and taking into account 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, and that at the room temperature. Thus we have a baseline characteristic of different classes of materials under the same—and easily obtained—environmental conditions.

TABLE 4.2. Numerical values of elongation at break, storage modulus, brittleness, and recovery for all materials tested.

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

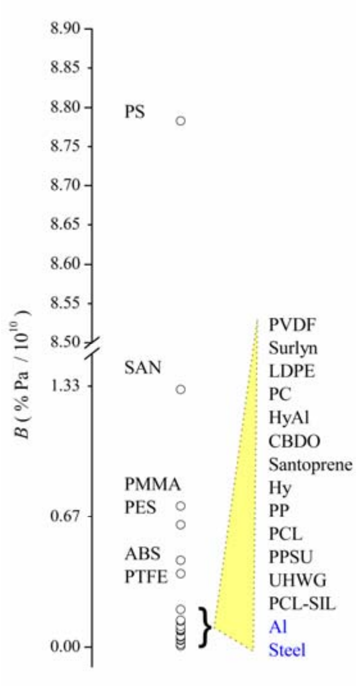


FIGURE 4.6. Brittleness scale of polymers and metals. *B* values calculated according to Eq. 2.9. Metals are indicated in blue text.

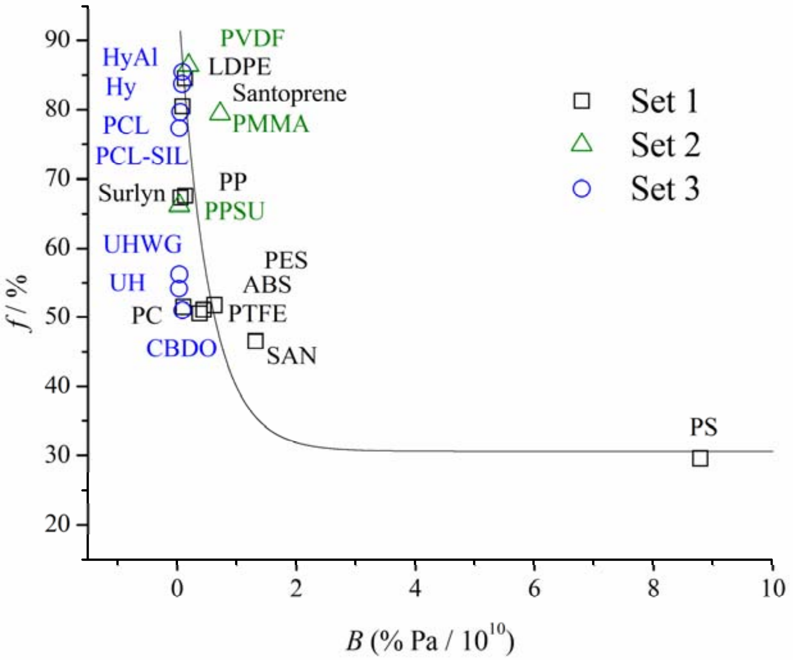


FIGURE 4.7. Percentage recovery as a function of *B* for materials in Sets 1, 2, and 3. The solid line represents an exponentially decaying function as a fit to the experimental data.

CHAPTER 5

OVERVIEW

5.1 Summary and Implications

We have tried to get to the bottom of the hardening in sliding wear: how frequent or infrequent it is, and what the mechanism is. Having confirmed (as demonstrated here and in [48,69,70,80]) that the phenomenon is universal except for PS, I asked for comments from others and received repeatedly the explanation "because PS is brittle". Asking further what “brittle” means, I found only hand-waving answers. It was this situation that behooved me to provide a quantitative definition of brittleness. The subsequent events—which led to my defining the term—are described in the preceding chapters.

The importance of wear and scratch resistance of polymers along with the time-dependent nature of these properties are highlighted along the way and also in recent articles that suggest new methods of *dynamic* nano-indentation. However, the values obtained from such methods are not yet widely understood or connected to other known properties. Quite a few elastic modulus results obtained from nano-indentation experiments are actually wrong. Oliver and Pharr developed a method of obtaining the modulus from nano-indentation experiments for materials which are fully elastic.[83] The method has been applied thoughtlessly to a variety of materials which do not fulfill that condition. Several research groups in various countries [84-86] have demonstrated how large errors result from the use of the Oliver and Pharr method outside of its legitimate application range. This of course by no means invalidates the nano-indentation technique, only some of the values calculated from it. Used correctly, the technique is well-regarded.

An article by Morel and Jardret on nano-indentation of PMMA concludes that brittle behavior in the scratch may be connected to tensile behavior.[87] This is interesting in that it supports my use of a tensile parameter in the definition of brittleness. It is worth noting however that even in their conclusion described above, Morel and Jardret are using hardness as a stand-in for brittleness.

From the standpoint of tribology, it is clear that both single scratch testing and sliding wear can give us substantial information about the viscoelasticity and wear of polymers. Connecting this to mechanical properties, however, provides a better understanding of how the bulk properties influence surface behavior. Moreover, the definition of brittleness defined here is simple, predictive, and applicable to a wide range of materials. Therefore, although the definition $B = 1/\varepsilon_b E'$ is not complex, it is functional which is advantageous to potential users.

Note that B allows utilization of ε_b values from tables or by individual testing. If data for ε_b are available, one needs only to calculate E' from DMA by 3-point-bending, a test which requires small amounts of material in an easily-attained sample shape. With regard to sliding wear tests, by conducting scans at a constant load, others can more readily execute similar tests avoiding different capacities of equipments to precisely control the force under progressive load tests.

It is appropriate here to consider then that there is a variety of ways to improve properties of PBMs—including improvement of tribological properties.[9,88-98] As I have mentioned before [77]:

> They include adding fillers or other dispersed phases [9,88-90,92,97,98]; irradiation [91,95]; sol-gel technology [93]; optimization of injection molding [94]; and development of methods to evaluate tribological properties for cylindrical surfaces [96]. For multiphase systems and composites, surface and interfacial tensions are important.[99]

Since the quantity B is determined by familiar mechanical parameters and then connected to sliding wear, it may be useful for developing PBMs with improved properties.

An insightful observation: Werwa [84] describes interviews he conducted with visitors to the Materials MicroWorld, a museum exhibit created by the Materials Research Society (MRS). Adults and children interviewed at the Maryland Science Center—where the exhibit was available for a time—used terms such as hardness, toughness and brittleness when answering questions and describing their impression from the exhibit.[84] Likewise, undergraduate students in an introductory Materials Science and Engineering course at University of North Texas used such terms even before mechanical properties were covered and available definitions discussed.[85] Those students also attended an MRS and US National Science Foundation exhibit called Strange Matter shown in Dallas, and they used terms from mechanics relying on the everyday meanings of the words.[85] We know from this and more then that the term "brittleness" has been long used by laymen even though no definition existed. My definition of brittleness appears to agree with the everyday meaning of the word as it is already used.

5.2 Future Work

While this work has examined a wide range of polymers within the broad categories thermoplastics and thermoplastic elastomers, the class of thermoset polymers has not yet been included. Thermosets are those polymers whose chains are chemically crosslinked: epoxy resins, some polyurethanes, and vulcanized rubber are common examples. The chemical crosslinks affect strongly chain mobility and viscoelasticity. However, the underlying dependence on free volume remains the same for thermosets as for thermoplastics. It will be interesting to see where on the scale of brittleness such materials lie.

Since the definition of brittleness described here has been applied to polymers and to metals, it deserves to be tested also for ceramic specimens. We have observed that the addition of ceramic particles to a polymer matrix may change the brittleness of the pure polymer. Whether it increases or decreases depends on multiple factors—particle dispersion, filler-matrix adhesion, the amount of filler added, etc.—and typically (but not always) elongation is reduced for polymer-ceramic composites. Ceramics by themselves are recognized as brittle materials, with most exhibiting little or no measurable elongation before break in tensile testing. In fact, a search of more than six thousand ceramic materials in the MatWeb database returns only 72 with reported values for ε_b, and most of those are not pure ceramics but some kind of alloy. High values for E' are expected and combined with very low elongation at break should result in relatively high values of B for ceramics.

However, 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 the equation defined here.

Considering issues of elongation, this work could also be further strengthened by obtaining ε_b values not from tables but for the all specimens tested by sliding wear and DMA. Another important consideration in this discussion of brittleness is the matter of scale with regard to scratch testing. While tensile testing and dynamic mechanical analysis probe the bulk properties of materials the diamond indenter of the scratch tester makes a relatively small contact with a material's surface. This becomes especially critical upon the addition of particulate matter into a polymer matrix (as in composites) when surface features are of similar size with the indenter. While a large probe could average out differences between materials, a smaller one such as the 200 μm radius tip used here can pick up a variety of surface features. Further, the introduction of particles into a polymer matrix is expected to affect the mode of deformation and also viscoelastic recovery. For comparability of sliding wear results then, especially for composites, the size of diamond tip used ought to be considered. It is possible that the same filler particles would yield a different outcome in sliding wear by probes of different radii.

A tangential question that arises from this work relates to UHMWPE. As mentioned earlier, processing of UH is difficult, and commercial products cannot be prepared by conventional injection molding but require processes such as ram extrusion, compression molding, and sintering. For the same reason, UH is not frequently blended with other materials; its viscosity and tendency to char at high temperatures discourage melt blending with other polymers, although this has been done.[100-102] Most reported instances of non-polymer composites (containing metallic or ceramic particles) of UH are for developing materials with specific conductive properties.[103-105] Typically the components are combined by simple mixing of powders or blending at elevated temperature in equipment such as a Brabender preparation station. In this work I have combined UH with ceramic particles in the presence of solvent and allowed dispersion by ultra-sonication. Here the concentration of filler is so small as to cause little change in the measured properties. However, no agglomeration of filler particles was observed by electron microscopy. Given the value of UHMWPE for multiple applications—biomedical implants, thermo-electric blends, and body armor to name a few—it would be valuable to identify what kind of properties could be achieved by introducing larger quantities of filler into UH by the method I have described.

Further, with regard to advancing tribology of polymers, the connection between sliding wear recovery and free volume described in Chapter 2 is significant. The linear relationship predicted deserves to be tested further using free volume data on even more PBMs. Nonetheless, establishing that changes in free volume play an important role in the surface and wear behavior of polymers contributes toward better understanding of the mechanisms that determine wear resistance.

A large body of sliding wear data has been generated for a wide variety of PBMs. It may be instructive to examine that data further in light of the chemical structures, chain types (linear or branched), crystallinity, and molecular weights of the respective materials. For instance, it has been demonstrated [106] that molecular weight affects the wear resistance and ductility (during fracture) of PS. Since both E' and ε_b are sensitive to the effects of changing molecular weight, one might compare a series of such materials by the new definition of brittleness.

Finally, in view of the importance brittleness plays in the performance and failure of plastics [38,41,58], it is to be expected that scientists and engineers will continue to investigate and try to better explain it. The definition of brittleness described herein has provided a quantitative measure for comparability that avoids qualitative assessments or complicated analyses. It provides a step for the advancement of better scientific definitions of physically observed phenomena.

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