Predicting Wear From Mechanical Properties of Thermoplastic Polymers

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The wear of polymer-based materials is connected to their brittleness. We have previously formulated a quantitative definition of brittleness in terms of elongation at break and storage modulus for thermoplastic polymers. We provide a formula connecting brittleness to viscoelastic recovery (healing) after sliding wear. Our model fits a selection of ten thermoplastics representing several classes of polymers with different chemical structures and mechanical properties. Now including polyvinylidene fluoride, poly(methylmethacrylate), and polyphenylsulfone, we demonstrate that from our formula we can predict the percentage recovery in sliding wear from our measure of brittleness. POLYM. ENG. SCI., 48:1982–1985, 2008. © 2008 Society of Plastics Engineers

INTRODUCTION

Polymer based materials (PBMs) continue to replace metals because they are lightweight, easy to process, and relatively inexpensive [1]. However, wear of polymers and PBMs contributes to significant financial loss in industry [2]. Understanding the tribology of polymers is difficult: time is not a variable for metals and ceramics; however, polymers are viscoelastic, thus their properties change with time. Indeed, most tribological models are developed for the behavior of metals [3].

Wear itself is difficult to define [4]. We have described the so-called sliding wear that occurs by repetitive scratching of material surfaces [5, 6]. In this situation resistance to wear is determined by evaluation of the residual depth R_h and percentage of viscoelastic recovery f that follow repetitive scratching by a microindenter. Sliding wear analysis has been used to evaluate the performance of dental materials [7] and engineering thermoplastics [6, 8, 9].

Despite increasing numbers of studies on tribology of polymers, a paucity of fundamental understanding and lack of predictability still plagues our ability to design new PBMs with lower wear. On the other hand, abundant data on mechanical properties of PBMs exists. Since macroscopic properties of any kind are dependent on molecular structure and interactions, we expect connections between mechanical and tribological properties.

In fact we have shown that for polymer blends containing carbon black, the concentration at which the static friction drops rapidly is the same at which the electrical resistivity falls sharply [10]. We have also demonstrated that viscoelastic recovery in sliding wear increases linearly with the free volume [11].

With these kinds of connections, we can begin to predict one type of property based on another. Moreover, it is clear that efficient use of PBMs depends in part on the ability to predict properties in advance and thereby to avoid developing products by trial and error.

EXPERIMENTAL

Materials

Data reported herein are for nine thermoplastic polymers used previously and described in [1] plus three additional polymers: poly(methylmethacrylate) (PMMA, RTP Company), polyphenylsulfone (Solvay Advanced Polymers, L.L.C.), and polyvinylidene fluoride (PVDF, Solvay Solexis, Inc.). Other polymers were polystyrene (PS, Aldrich Chemicals Company), polycarbonate (Dow Chemical Company), acrylonitrile/butadiene/styrene copolymer (ABS, Dow Chemical Company), polytetrafluoroethylene (PTFE or Teflon[®], Dow Chemical Company),

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isotactic polypropylene (PP, Huntsman), low density polyethylene (LDPE, Huntsman), polyethersulfone (PES, Solvay Engineered Plastics), SantopreneTM (a copolymer of PP and ethylene-propylene-diene-monomer, Advanced Elastomer Systems), styrene/acrylonitrile copolymer (SAN or Luran[®], BASF, Ludwigshafen/Rhein), and Surlyn[®] 8140 (a copolymer of ethylene and methacrylic acid, E.I. du Pont de Nemours, Wilmington, DE). Molecular weights are not usually provided by suppliers; the materials used were unfilled injection-molding grade polymers.

Sliding Wear

As described in another paper [11], siding wear tests were performed on a micro scratch tester (MST from CSM Instruments, Neuchatel, Switzerland) in multiple scratch mode. The instrument and procedure have been described previously [6, 10, 12]. The test consists of 15 scratches by a diamond tip along the same groove. Each material was tested under constant loads of 5.0, 10.0, and 15.0 N at room temperature (25°C). Scratch speed was 2.5 mm/min, and the total scratch length was 5.0 mm. Values for penetration depth R_p and residual depth R_h were determined from the midpoint (2.5 mm along the scratch length). The percentage of viscoelastic recovery fwas calculated from R_p and R_h for the 15th scratch using the definition formulated in [12]:

$$f = \left[\left(R_{\rm p} - R_{\rm h} \right) \times 100\% \right] / R_{\rm p} \tag{1}$$

Here values of f for PMMA, PPSU, and PVDF are from sliding wear under a 5 N applied load (based on the fact that f is independent of load within the range tested [11]).

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed as before [11] to determine storage E' and loss E'' moduli. Measurements were recorded using the DMA7e apparatus (Perkin Elmer Co.) by 3-point bending in temperature scan mode at the frequency of 1.0 Hz. As discussed in the literature [13–15], DMA is an effective means to evaluate viscoelastic properties of PBMs based on imposing a sinusoidal stress at a particular frequency as a function of time. A phase shift in the strain responses of the material correlate to the solid-like (E') and liquid-like (E'') components of the material's behavior. Thus DMA provides a fundamental description of polymer viscoelasticity.

Elongation at Break

As we did previously in [11], values for elongation at break $\varepsilon_{\rm B}$ for PMMA, PPSU, and PVDF were obtained from the MatWeb Online Materials Database (www.

TABLE 1. Tabulated values for elongation at break ε_{b} , storage modulus E', viscoelastic recovery f, and brittleness B.

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

* Data for Set 1 appears also in our previous publication [11].

matweb.com). Averages were taken where a range of values was reported.

Calculation of Brittleness

Brittleness *B* of PMMA, PPSU, and PVDF was calculated using the equation developed by us in 2006 [11]:

$$B = 1/(\varepsilon_{\rm b} E') \tag{2}$$

We have used units of % for ε_b and Pa for E'. Values of *B* are reported in Table 1.

RESULTS AND DISCUSSION

We need still improvement in wear of PBMs, and this requires better understanding. For instance, fiber-reinforced plastics are important class of PBMs. Fibers are added to improve not only mechanical properties but also tribological ones. However, wear is not always decreased by fiber reinforcement; in fact a contrary effect has been reported by Fallon and Eiss Jr [16]. Therefore, we sought to establish connections between mechanical and tribological properties, relating them to the physical nature of the corresponding materials.

As mentioned earlier, we have shown that recovery in wear f increases with the free volume [11]. Now we have defined brittleness for thermoplastic polymers in a way that agrees with the accepted meaning of the word. Figure 1 shows the dependency of viscoelastic recovery on brittleness. PS has high brittleness and a low percentage recovery. Other materials with lower brittleness exhibit higher viscoelastic recovery and thus lower wear. The scatter of values from the best fit line is expected given that data for elongation at break are averages from tables and not from measurements on our material specimens. The relationship between f and B (see Fig. 1) is in the form of an exponential decay.

It has been suggested that materials such as PMMA and PPSU are brittle. What we observe, however, is that

these materials are frequently used in high-performance applications. Our results agree with the observed use of these materials, namely that they do not have high values of *B* and show decent behavior in sliding wear. Further, a phenomenon of strain hardening has been observed for plastics subjected to sliding wear tests [5, 6]. Among a large number of neat polymers and composites tested in our laboratory, PS is the only one we have discovered that does not show strain hardening [8, 9]. The phenomenon is confirmed for PMMA, PPSU, and PVDF. As seen in Fig. 2, after repetitive scratches along the same groove, strain hardening results in a plateau of both the penetration and residual depths for these materials.

In 1997 Quinn and Quinn proposed a new index of brittleness-based on the hardness, Young's modulus, and fracture toughness-for ceramics [17]. The use of the Young modulus precludes the use of the index for viscoelastic materials. By contrast, our definition of brittleness formulated in 2006 [11] is general. In the present work our definition has been tested through evaluation of several additional thermoplastic polymers. Sliding wear profiles for so-called brittle PMMA and PPSU do not in fact behave like brittle PS but instead show strain hardeningas do other nonbrittle engineering thermoplastics. There exists a correlation between viscoelastic recovery and brittleness such that recovery decreases with increasing brittleness. An expansion of this model to incorporate behavior of thermosetting polymers and composite materials is planned.

There is a variety of ways to improve properties of PBMs-including improvement of tribological properties [18–29]. They include adding fillers or other dispersed phases [18–20, 22, 25, 28, 29]; irradiation [21, 26]; solgel technology [23]; optimization of injection molding [24]; and development of methods to evaluate tribological properties for cylindrical surfaces [27]. For multiphase systems and composites, surface and interfacial tensions are important [30]. Since our definition of brittleness is



FIG. 1. Percentage of viscoelastic recovery f in sliding wear obtained from Eq. 1 as a function of brittleness B calculated from Eq. 2.



FIG. 2. Sliding wear profiles for (a) PMMA, (b) PVDF, and (c) PPSU. Penetration depth R_p and residual depth R_h are plotted versus the number of scratches under a 5.0 N applied load.

based on common mechanical behavior and also connected to wear behavior, it is useful for developing PBMs with improved properties.

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