Mechanochemical Aspects of Repetitive Impacts and Sliding on Polymers

E. SACHER, P. A. ENGEL, and R. G. BAYER, *Materials and Engineering Analysis, IBM System Products Division, Endicott, New York 13760*

Synopsis

Scattered data exist in the literature on the chemical reactions which occur during mechanical contact. It is our contention that these reactions occur as a direct result of the high temperatures generated at the contact interface, due to the dissipation of mechanical energy. A theoretical analysis is used to identify and rank the various sources of heat generation during repetitive impact or sliding. New data, on both filled and unfilled polymers and elastomers, supported by data from the literature, are used to show that the resultant temperature rise causes reactions at the interface; the extents of these reactions depend on the polymer structure and the magnitude of the temperature rise. Several ways of reducing the magnitude of this temperature rise are discussed.

INTRODUCTION

Over the years we have from time to time observed interfacial chemical reactions during mechanical contact. These reactions have been found, by us and others, to occur on both polymeric and metallic materials. Invariably, they either show evidence of high temperatures (charring, flow, dehydrohalogenation) or show chemical products which are normally produced at high temperatures (metallic oxides).

Mechanochemical reactions are those reactions which are initiated by the dissipation of mechanical energy. Chemical reactions may occur at the interface between contacting solids, as when friction polymers are produced in lubricated systems.[1-3] Surface techniques, such as ESCA, Auger spectroscopy, and surface tension measurements have shown that bonding occurs between the polymer surface layers and a contacting metal,[4-6] even when the contact is static.[4] These bonds may possibly initiate the reactions which lead to friction polymers,[1-3,*] charring,[7] and dehydrohalogenation,[7] although they probably do not play a major role. This is because mechanochemical reactions involve far more than the surface layers of both the polymer and the contacting metal and appear to require heat generation. In the absence of *sliding* contact,[1-3,7] these same reactions occur only at much higher temperatures, implying that such contacts generate high temperatures at the interface; this has been verified in several cases.[8-14] (We omit from consideration the high-load, high-strain-rate processes such as cutting, milling, mastication, and fracture, which are known[11,15-22] to produce free radicals through homolytic scission.)

Although a basic ignorance exists concerning those chemical reactions which occur during the wear process,[23] one can at least identify the mechanical processes

---

*Friction polymers can form during low speed sliding in the presence of organic liquids and vapors. Their formation is thought to initiate through absorption onto the metals, homolytic scission during shear, followed by free radical polymerization.

0021-8995/79/0024-1503$01.00

which lead to a temperature increase; calculations and experimental verification then permit them to be ranked as to the magnitude of the temperature increase expected.   A knowledge of the mechanical properties of the polymer at the interface[24–26] will permit the evaluation of those temperature-dependent ultimate properties which govern its use (i.e., stress-strain behavior, ultimate strength, impact properties, and long-term behavior).   Knowledge of the chemical properties of the polymer will permit the evaluation of those predominantly degradative reactions which may occur under use conditions.[27,28]

It was our initial purpose to investigate the mechanochemical effects of several polymers of current interest, emphasizing both sliding and impacting conditions. Shortly after the study began, it became apparent that there were several mitigating effects, which could be used either adversely or favorably to influence the results.   Both the present results and those already found in the literature are used to discuss these mitigating effects.

EXPERIMENTAL

The sliding experiments were carried out on a modified Bowden-Leben apparatus,[29] using a 1.27-cm diameter spherical slider of 52100 steel having a peak-to-valley roughness of <0.05 μm.   The impacting experiments used a pivotal hammer system,[7] operating at 50 Hz and having a 0.092-cm-wide hammer with a 0.3-cm-long face with a cylindrical radius of 3.5 cm.   The x-ray fluorescence detection of chloride was carried out with a Kevex model 3000 energy-dispersive analyzer, using Fe 55 as the source.

The polymer samples used were 127-μm DuPont Kapton 500 H polyimide film, 124-μm Bayer Makrofol N polycarbonate film, and 3200-μm General Electric Lexan 9400 polycarbonate sheet.   The elastomers used were DuPont Adiprene L-167 and Hytrel 6345, Allied Multrathane F242, Mobay Texins 355D, 480A, and 591A, and Uniroyal Roylar ED-65; all were 600 μm thick and had been cured according to manufacturer's specifications.

RESULTS

The following results show that while mechanochemical effects certainly occur, they may be mitigated by other phenomena.

Energy Dissipation Through Heat and Fracture

DuPont's Kapton polyimide film is a high-temperature-stable dielectric[7,30,31] with a glass transition temperature in excess of 500°C.   Under a 1-kg load on a 1.27-cm diameter spherical slider of 52100 steel, 7000 pases at an an average velocity of 15 cm/sec showed evidence of plastic flow, as seen in Figure 1.   Under identical conditions, the same thickness (127 μm) of polycarbonate film showed substantially less flow (Fig. 2) but showed lateral cracks.   This result is surprising because not only does polycarbonate have a significantly lower glass transition temperature of 150°C,[32] but its coefficient of friction (as determined by us for loads up to 1000 g and average velocities up to 13.6 cm/sec on a 1.27-cm diameter spherical slider of 52100 steel) is in the range 0.58–0.65, twice as high as that of polyimide.[30]   Figure 3 shows the result of reduced average velocity: an increase

Fig. 1. Wear track of 127-μm DuPont Kapton H polyimide, 90×, after 7200 traces of a 1.27-cm diameter 52100 steel slider under a 1-kg load at 24°C, 35% R.H. The average velocity was 15 cm/sec.

Fig. 2. Wear track of 124-μm Bayer Makrofol N polycarbonate, 500×, after 5200 traces of a 1.27-cm diameter 52100 steel slider under a 1-kg load at 24°C, 35% R.H. The average velocity was 15 cm/sec.

in the amount of flow and a decrease in the amount of cracking. This suggests that the higher shear resistance of polycarbonate causes the dissipation of some of the energy of the slider in fracture.

Detrimental Effect of Contaminant Ions

An interesting demonstration of the high temperatures attained due to fretting motion may be seen in some of our recent work on the impacting of 600-μm-thick polyurethane elastomers. Using a 50-Hz repetition rate pivoted hammer system

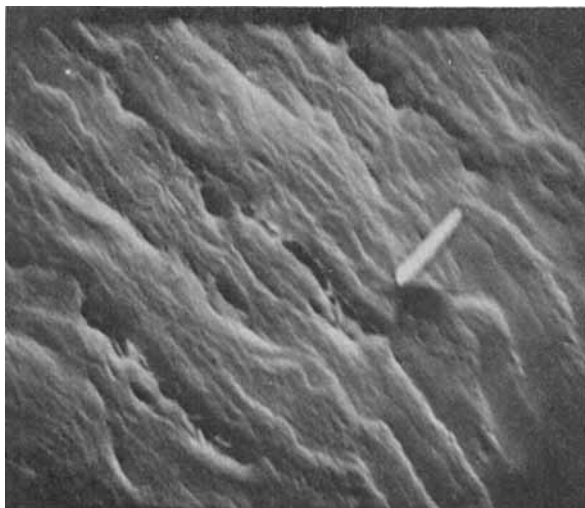Fig. 3. Wear track of 124-μm Bayer Makrofol N polycarbonate, 500×, after 5200 traces of a 1.27-cm diameter 52100 steel slider under a 1-kg load at 24°C, 35% R.H. The average velocity was 4 cm/ sec.

previously described,[7] samples of DuPont Adiprene L-167 and Hytrel 6345, Allied Multrathane F242, Mobay Texins 355D, 480A, and 591A, and Uniroyal Roylar ED-65 were impacted at hammer impact velocities of <380 cm/sec. In the case of both DuPont materials, 3×10^6 impacts produced red iron oxide (rust) on both the hammer and the contacted areas of the elastomer; further, when the underside of the elastomer rested against a steel substrate, that interface rusted as well. The extent of rusting, at a constant 3×10^6 impacts, increased with hammer velocity.

X-ray fluorescence showed that both the DuPont materials contained chloride ions. (The Multrathane was also found to contain chloride but at a qualitatively far lower concentration than either DuPont material.) Although MOCA, which contains covalently bound chloride, is used to catalyze the Adiprene, some hydrolyzable chloride must be available in both materials, or must be produced on impact from covalently bound chloride. Under these circumstances, the following heterogeneous chemical reaction may occur[33-35]:

$$Fe + Cl^- \rightarrow FeCl_2 \xrightarrow[\text{oxygen}]{\text{water}} Fe_2O_3 + Cl^-$$
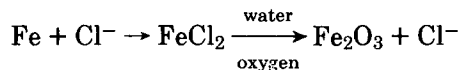
The first stage normally occurs at elevated temperatures. Note that chloride ion is released for further reaction with iron. That fretting motion is the prime cause of the rusting is clear from the fact that when the undersides of the DuPont materials were bonded to the substrate, rust formation was eliminated at that interface.

Furthermore, both DuPont materials were placed between steel plates in a controlled environment at 90°C/90% R.H. Even after 1 week, no rust could be detected. Since the literature indicates that elevated temperatures are required for $FeCl_2$ formation,[33-35] the impacted polyurethane–metal interfaces must have been substantially hotter than 90°C.

Effect of Thickness

Impact wear behaviors for thick and thin samples of polycarbonate were clearly distinguishable. In a previous study,[7] a 64-μm (thin) sample of steel-supported Bayer Makrofol KG polycarbonate was impacted with a pivotal hammer system. Charring occurred after 10^7 impacts. Thermogravimetric analysis led to the conclusion that the interfacial temperature exceeded 400°C. When we impacted a 3200-μm (thick) sample of General Electric Lexan 9400 polycarbonate under identical conditions, both brittle fracture and plastic flow were observed, without charring (Fig. 4).

DISCUSSION

Mechanical Heat Sources During Impacting

A recent paper[7] discussed the various mechanical heating sources during repetitive impact. In the order of increasing temperature, these were identified as partial slip, viscoelastic effects, and fretting motions.

Partial slip occurs when the hammer impacts the sample. Tangential motions occur at some locations on the interface, leading to a differential displacement, or slip. The energy dissipated per impact per width of cylindrical hammer, U, is[36]

$$U = f(\mu)E'b^4/R^2 \tag{1}$$

where $f(\mu)$ is a function of the coefficient of friction, E' is the tensile modulus evaluated at the temperature and equivalent frequency of the impact, b is the half-contact length of the cylinder, and R is its radius. Under most impacting conditions, the energy dissipated was too low for a measurable temperature rise.
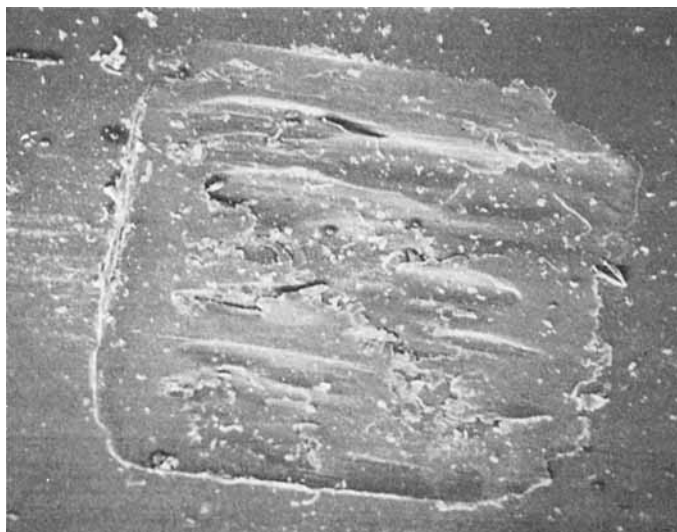

Fig. 4. Impact scar of 3200-μm General Electric Lexan 9400 polycarbonate, 50×, after 10^7 impacts of a 0.0915-cm-wide × 0.203-cm-long hammer with a cylindrical radius of 3.49 cm, an effective mass of 0.546 g, and a velocity of 380 cm/sec, operating at 50 Hz at 24°C, 35% R.H.

Viscoelastic effects occur when mechanical impacts result in viscous energy dissipation. The energy dissipated per cycle per unit volume, Q, is[37,38]

$$Q \approx \pi E'' \epsilon / 2 \tag{2}$$

where E'' is the tensile loss modulus evaluated at the temperature and equivalent frequency of the impact and ϵ is the peak strain. The temperature rise in the sample, δT, is[7,39]

$$\delta T = \frac{2qh}{K} \left[\frac{x}{2h} - \left(\frac{x}{2h} \right)^2 \right] \tag{3}$$

where q is the internally generated heat ($= Q \times n$, where n is the impact rate), h is the sample thickness, and K is the coefficient of thermal conductivity. The maximum temperature rise occurs at the sample surface ($x = h$). Depending on the conditions of impact, for highly viscoelastic elastomers such as butyl and neoprene rubbers a temperature rise of some tens of degrees centigrade is expected,[39] while for semicrystalline polymers, the temperature rise is expected to be significantly lower because of their lower viscous damping.

Fretting motions are those small-amplitude lateral motions which occur during impact because of the high-frequency lateral hammer vibrations. Our hammer systems have such vibrational frequencies of ~ 1 kHz. Because fretting motions occurred during impact, a form of repetitive sliding *under variable load* was involved. The temperature rise due to this effect is[40]

$$\delta T \approx 2\mu P_0 v / 3\pi a K \tag{4}$$

where μ is the coefficient of friction, P is the maximum impact force, v is the average velocity of the lateral vibration during contact, and a is the equivalent contact radius. Depending on the measured or estimated values used in the equation, temperature rises approaching 1000°C are predicted, and actual temperature rises of about 200°C have been measured during sliding.[41] This should not be surprising, since one can expect gross heat generation due to power losses during sliding (i.e., friction force × velocity), which includes the shearing fracture of interfacial adhesion sites. Such fracture is expected to produce such elevated temperatures, since the temperature rise at the tips of fast-moving cracks has been found to approach 400°C in polymers[42] and is substantially higher in inorganic materials.[43] These power losses are one source of the well-known flash temperature.[44,45]

It has been shown[1-3] that the buildup of friction polymers during metal-to-metal contact is due uniquely to sliding, indicating that fretting motion in metal-to-metal contact is capable of producing high temperatures. In spite of this, and with the exception of Feng and Uhlig (see appropriate references in Ref. 9), temperature effects on the chemical reactions occurring during metal-to-metal fretting are generally disregarded, as may be seen in a recent review.[9] However, a study on the wear rate of unlubricated sliding of metals[46] considering the various iron oxides known to form at specific temperatures, estimated the temperature rise above ambient as 680°C for pure iron at the sliding interface. Furthermore, recent experiments on metal–polymer and glass–polymer sliding[12] indicated that high temperatures are also attained at these interfaces, although the metal tends to conduct much of this away.

The various mechanical heat sources have been considered separately, although, under actual conditions, they will occur simultaneously. For some polymers, E'' has a positive temperature coefficient under impacting conditions,[7] initiating a self-perpetuating temperature rise which could account for high temperatures even when fretting motions are minimized. These and the previously mentioned power losses are the sources of the flash temperature.[44,45]

Mechanical Heat Sources During Sliding

Superficially, gross sliding may be thought of as being similar to fretting motion, in that they both occur in the plane of contact. Fretting, however, is associated with small-amplitude oscillations in the plane of the contact and results in a somewhat different mechanism, particularly since the wear debris is more likely to stay within the contact area. Thus while fretting motion and sliding may be analogous for the purpose of discussion, the analogy is limited.

The polymer in front of a moving slider is compressed until the slider passes and the compression is relaxed,[47] giving rise to both viscoelastic and sliding effects. Sliding effects overshadow viscoelastic effects, since the latter are observable only when shear resistance is made extremely small, as in the case of a rolling contact.[47–53]

Sliding effects were considered in the discussion on fretting motions. We have estimated our average fretting velocities [v in eq. (4)] as about 2 m/sec, and it is interesting to note that at the same velocity, disc-on-disc sliding of metal against polyimide produced temperature rises of about 200°C.[41] Even at a velocity of 0.3 m/sec, sliding for a short period of time caused the appearance of unsaturation in polyethylene.[54]

Effect of Heat on Polymer Surfaces

The effect of mechanically generated heat depends on the individual polymer and the reactions it can undergo at the temperature attained. For example, polyvinyl fluoride[7] loses hydrogen fluoride at an estimated temperature >300°C, as evidenced by an infrared-observed gain in unsaturation at 1710, 1505, 760, and 715 cm^{-1} and a loss of fluoride at 1495 cm^{-1}. Similarly, polyethylene[54] loses hydrogen to produce unsaturation at 996, 992, 909, and 889 cm^{-1} but, being more easily oxidized than polyvinyl fluoride, shows evidence of some oxidation in the multiple peaks appearing in the region between 1740 and 1710 cm^{-1}.

Some Mitigating Effects

Stress Level

The stress levels on impacting thin films have previously been considered.[7] There, the nearly constant wear rate found with increasing peak force has been explained in terms of a constant, uniform flow pressure.[55] That is, as the peak force is increased, the hammer contact length increases linearly, maintaining essentially constant contact stress conditions. (The contact force is linearly related to the contact length of the cylindrical indenter for a constant average pressure.[7]) However, when the contact length exceeds the hammer width, increasing the load increases the contact pressure (overstress), and when the impact

strength of the material is exceeded, rapid mechanical deterioration follows. The absence of observable thermal effects in such cases shows that little or no energy was dissipated as heat.

A similar effect is found in sliding; when the contact length exceeds the width of the slider required for elastic contact, plowing and cutting are observed. Due to frictional effects, the contact stress may exceed the tensile stress of the polymer, even when the elastic slider width is not exceeded. Although not strictly applicable to the subject of this paper, this topic is included here because it illustrates the cause of the lateral cracks in polycarbonate found in Figure 3.

Thus, the yield stress σ_y of polycarbonate is 62 MPa.[32] For a 1-kg load on a 1.27-cm diameter steel slider, Hertzian analysis shows[56] that the maximum contact pressure p_{max}, is

$$p_{max} = \frac{6}{\pi} \left(\frac{E_r}{6\pi R} \right)^{2/3} P^{1/3} \tag{5}$$

where E_r is the reduced tensile modulus, R is the slider radius, and P is the load. For polycarbonate, $p_{max} = 70$ MPa. For a coefficient of friction of 0.6, the normal stress in the direction of motion σ_x, is[57,58] $1.2 \times p_{max}$, or 84 MPa; this exceeds σ_y, and fracturing is expected. This occurs, as seen in Figure 3. Reducing the load to 10 g noticeably reduces the amount of fracture (Fig. 5).

Chemical Environment

As discussed earlier, the presence of certain ions may prove detrimental. However, the chemical environment may also include the surrounding atmosphere.

While additives are generally added to a polymer in order to extend its use, these may not be stable at the very high temperatures of the contact interface, leading to degradative reactions[27,28] which further physically weaken the contact interface. This may be mitigated, as discussed in the following subsection.
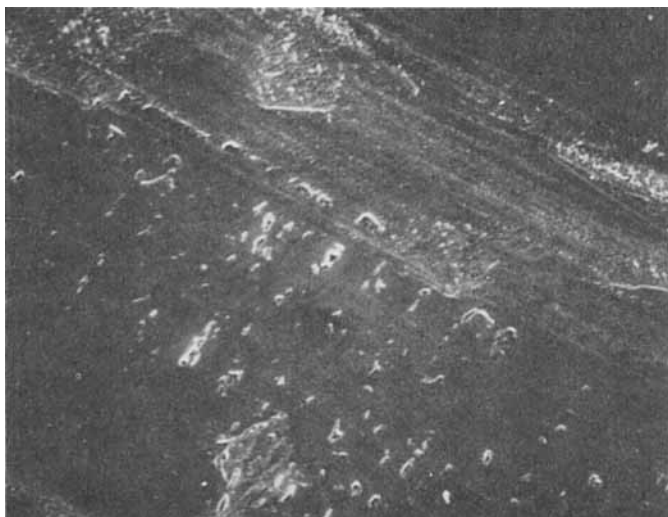

Fig. 5. Wear track of 124-μm Bayer Makrofol N polycarbonate, 500×, after 5200 traces of a 1.27-cm diameter 52100 steel slider under a 10-g load at 24°C, 35% R.H. The average velocity was 4 cm/sec.

Thickness

The effect of sample thickness manifests itself mainly in the case of impacting, where deformation strongly depends on the local stiffness of the material under the conditions of impact. For metal-supported elastomers, the dramatic decrease in peak impact force with increasing thickness has recently been demonstrated.[59] In the case of sliding, increased sample thickness results in increased resistance to motions in the interfacial plane, while in the case of impacting, fretting motions and the heat they generate are reduced. (For small oscillations, a thicker polymer sample can develop better adhesion, giving less slip.) One should also note, however, that metal-supported thinner samples may achieve lower temperatures through better heat conduction.

These failure patterns show the influence of the contact stress system; the distribution of tensile stresses in a thicker sample is conducive to the formation of surface and subsurface cracks, which ultimately lead to the observed wear scar. The absence of charring in Figure 4 indicates that temperatures did not exceed 400°C, while the presence of brittle fracture indicates that the temperature of the impacted area did not exceed the T_g, 150°C.[32]

Orientation

While this was not considered earlier, it is considered here because of its important mitigating effect. The effect of orientation on sliding seems to have first been noticed during experiments on polytetrafluoroethylene.[60,61] The initial coefficient of friction, ~0.2, fell to ~0.06, commensurate with the buildup of a chemically degraded[62] transfer film. Electron diffraction studies showed the transfer film to be oriented in the sliding direction, with sliding occurring at the interface between the transfer film and the bulk polymer. The reduction in the coefficient of friction has been postulated[60,61] to be due to the smooth molecular profile of the oriented transfer film. This has been confirmed by the finding[61] that high-density (i.e., linear) polyethylene gives essentially the same results, while low-density (i.e., branched) polyethylene behaves like a "normal" polymer. Recent work[63] indicates that (presumably oriented) transfer films provide wear protection, in that the presence of such a film increases the ambient temperature at which severe wear begins. Since this phenomenon is found for Nylon 66 and DuPont's Delrin polyoxymethylene, as well as for PTFE-filled Delrin, it may be that transfer films in general provide a lubricating effect. The formation of such films is strongly influenced by the ability of the polymer to bond to the metal surface.[64] The ambient temperature at which severe wear begins may then signal the loss of transfer film adhesion.

The "smooth-profile" concept can be extended to a macroscopic scale in the case of fiber-filled polymers. Several recent papers[65,66] on oriented fillers (see Fig. 6) confirm that in the plane of fiber orientation (plane ABEF in Fig. 6), the coefficient of friction and the specific wear rate were both found to be directly related to the angle between the sliding direction and the fiber orientation, being lowest when they coincide. Sliding perpendicular to the plane of fiber orientation (plane ABCD in Fig. 6) gave still lower values. The specific wear rate was also inversely dependent on the modulus of the composite, rather than of the resin or fiber, separately. Similar behavior has been observed[67] in metallic wear under lubrication: sliding parallel to the surface roughness ridges produced by finishing caused significantly less wear than sliding perpendicular to them.
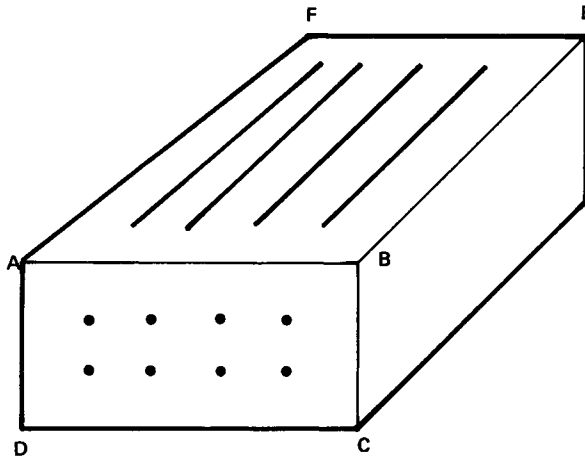
Fig. 6. The planes in an oriented, fiber-filled composite.

This suggests that when impacting in the fiber plane, fretting motion in the fiber direction will lead to lower wear rates. Such has been found to be the case for oriented carbon fibers.[68] However, impacting perpendicular to the fiber plane gave a somewhat higher wear rate than that in the fiber direction; this is probably due to the low compressive strength of the carbon fibers used. This interpretation is based on a study of liquid impact *across the faces* of oriented carbon fiber-reinforced plastics[69]: the erosion was independent of the resin or of the amount of fiber loading, depending only on fiber compression fatigue.

CONCLUSIONS

Mechanochemical effects occur because of a temperature rise due to the conversion of mechanical energy into heat. The major source of this heat has been shown to be due to in-plane motions at the contact interface. Several mitigating effects have been found to reduce or eliminate this temperature rise and its resultant detrimental effects: the least heat generation is predicted to occur on thicker samples, at low stress levels, where in-plane motions are confined to the direction of orientation.

References

1. H. W. Hermance and T. F. Egan, *Bell Syst. Tech. J.,* **37,** 739 (1958).
2. W. E. Campbell and R. E. Lee, Jr., *ASLE Trans.,* **5,** 91 (1962).
3. R. S. Fein and K. L. Kreuz, *ASLE Trans.,* **8,** 29 (1965).
4. D. H. Buckley and W. A. Brainard, in *Advances in Polymer Friction and Wear,* L.-H. Lee, Ed., Plenum, New York, 1974, p. 315.
5. R. F. Roberts and H. Schonhorn, *Polym. Prepr.,* **16**(2), 146 (1975).
6. R. F. Roberts, F. W. Ryan, H. Schonhorn, G. M. Sessler, and J. E. West, *J. Appl. Polym. Sci.,* **20,** 225 (1976).
7. R. G. Bayer, P. A. Engel, and E. Sacher, *Wear,* **32,** 181 (1975).
8. B. Maxwell, *J. Polym. Sci., Part C,* **9,** 43 (1965).
9. P. L. Hurricks, *Wear,* **15,** 389 (1970).
10. V. V. Boldyrev and E. G. Avvakumov, *Russ. Chem. Rev.,* **40,** 847 (1971).
11. A. Casale, R. S. Porter, and J. F. Johnson, *Rubber Chem. Technol.,* **44,** 534 (1971).
12. K. Tanaka and Y. Uchiyama, in *Advances in Polymer Friction and Wear,* L. H. Lee, Ed., Plenum, New York, 1974, p. 499.
13. P. G. Fox, *J. Mater. Sci.,* **10,** 340 (1975).

14. A. Casale, *J. Appl. Polym. Sci.,* **19,** 1461 (1975).

15. R. J. Ceresa and W. F. Watson, *J. Appl. Polym. Sci.,* **1,** 101 (1959).

16. F. Bueche, *J. Appl. Polym. Sci.,* **4,** 101 (1960).

17. F. Bueche, *J. Appl. Polym. Sci.,* **4,** 107 (1960).

18. S. E. Bresler, S. N. Zhurkov, E.N. Kazbekov, E. M. Saminskii, and E. E. Tomashevskii, *Rubber Chem. Technol.,* **33,** 462 (1960).

19. W. F. Watson, in *Chemical Reactions of Polymers,* E. M. Fetts, Ed., Interscience, New York, 1964, p. 1085.

20. P. Ya. Butyagin, A. M. Dubinskaya, and V. A. Radstig, *Russ. Chem. Rev.,* **38,** 290 (1969).

21. J. Tino, J. Placek, and F. Szocs, *Eur. Polym. J.,* **11,** 609 (1975).

22. M. Sakaguchi and J. Sohma, *Polym. J.,* **7,** 490 (1975).

23. M. O. W. Richardson, *Wear,* **17,** 89 (1971).

24. J. D. Ferry, *Viscoelastic Properties of Polymers,* Wiley, New York, 1961.

25. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids,* Wiley, New York, 1967.

26. I. M. Ward, *Mechanical Properties of Solid Polymers,* Wiley-Interscience, New York, 1971.

27. M. B. Neiman, Ed., *Aging and Stabilization in Polymers,* Consultants Bureau, New York, 1965.

28. L. Reich and S. S. Stivala, *Elements of Polymer Degradation,* McGraw-Hill, New York, 1971.

29. R. G. Bayer, W. C. Clinton, C. W. Nelson, and R. Schumacher, *Wear,* **5,** 378 (1962).

30. R. G. Bayer and E. Sacher, *Wear,* **37,** 15 (1976).

31. E. Sacher, *IEEE Trans. Electr. Insul.,* **EI-13,** 94 (1978).

32. H. Schnell, *Chemistry and Physics of Polycarbonates,* Interscience, New York, 1964, Chap. 5.2.

33. N. V. Sidgwick, *The Chemical Elements and Their Compounds,* Clarendon Oxford, 1950, p. 1331.

34. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Interscience, New York, 1962, Chap. 29.23.

35. J. J. Lagowski, *Modern Inorganic Chemistry,* Dekker, New York, 1973, Chap. 16.3.1.

36. P. A. Engel and H. D. Conway, *IBM J. Res. Dev.,* **15,** 116 (1971).

37. Reference 24, p. 433.

38. Reference 25, p. 520.

39. P. A. Engel, *Impact Wear of Materials,* Elsevier, New York, 1976, Chaps. 3.8 and 10.4

40. R. Holm, *J. Appl. Mech.,* **19,** 369 (1952).

41. H. L. Price and H. D. Burks, *Polym. Eng. Sci.,* **14,** 288 (1974).

42. K. N. G. Fuller, P. G. Fox, and J. E. Field, *Proc. R. Soc. London, Ser. A* **341,** 537 (1975).

43. P. G. Fox and J. Soria-Ruiz, *Proc. R. Soc. London, Ser. A* **317,** 79 (1970).

44. J. F. Archard, *Wear,* **2,** 438 (1958/59).

45. H. Blok, *Wear,* **6,** 483 (1963).

46. T. F. J. Quinn, *Wear,* **18,** 413 (1971).

47. D. Tabor, in *Advances in Polymer Friction and Wear,* L.-H. Lee, Ed., Plenum, New York, 1974, p. 5.

48. D. G. Flom, *J. Appl. Phys.,* **32,** 1426 (1961).

49. K. G. McLaren and D. Tabor, *Nature,* **197,** 856 (1963).

50. K. A. Grosch, *Nature,* **197,** 858 (1963).

51. K. A. Grosch, *Proc. R. Soc., London, Ser. A* **274,** 21 (1963).

52. K. C. Ludema and D. Tabor, *Wear,* **9,** 329 (1966).

53. A. D. Roberts, *Tribol. Int.,* **9,** 75 (1976).

54. V. A. Belyi, A. I. Sviridyonok, V. A. Smurugov, and V. V. Nevzorov, in *Wear of Materials, 1977,* W. A. Glaeser, K. C. Ludema, and S. K. Rhee, Eds., American Society of Mechanical Engineers, New York, 1977, p. 526.

55. D. M. Marsh, *Proc. R. Soc. London, Ser. A* **279,** 420 (1964).

56. Reference 39, Chap. 2.3.

57. G. M. Hamilton and L. E. Goodman, *J. Appl. Mech.,* **33,** 371 (1966).

58. Reference 39, Chapters 2.3, 3.5 and Appendix 2.

59. P. A. Engel and R. C. Lasky, *Exp. Mech.,* **17,** 97 (1977).

60. C. M. Pooley and D. Tabor, *Proc. R. Soc. London, Ser. A,* **329,** 251 (1972).

61. B. J. Briscoe, C. M. Pooley and D. Tabor, in *Advances in Polymer Friction and Wear,* L.-H. Lee, Ed., Plenum, New York, 1974, p. 191.

62. B. C. Arkles and M. J. Schireson, *Wear, 39,* 177 (1976).

63. S. H. Rhee and K. C. Ludema, in *Wear of Materials 1977,* W. A. Glaeser, K. C. Ludema, and S. K. Rhee, Eds., American Society of Mechanical Engineers, New York, 1977, p. 482.

64. R. G. Bayer and J. L. Sirico, *IBM J. Res. Dev., 22,* 90 (1978).

65. N.-H. Sung and N. P. Suh, in *35th ANTEC,* Society of Plastics Engineers, Montreal, 1977, p. 311.

66. T. Tsukizoe and N. Ohmae, in *Wear of Materials 1977,* W. A. Glaeser, K. C. Ludema, and S. K. Rhee, Ed., American Society of Mechanical Engineers, New York, 1977, p. 518.

67. R. G. Bayer and J. L. Sirico, *Wear, 35,* 251 (1975).

68. N. Ohmae, K. Kobayashi, and T. Tsukizoe, *Wear, 29,* 345 (1974).

69. N. L. Hancox, *Wear, 23,* 71 (1973).