

# Relation Between Strain Hardening and Wear Resistance of Polymers

Y. J. Mergler,<sup>1,2</sup> R. P. Schaake<sup>1,2</sup>

<sup>1</sup>TNO Industrial Technology, Surface Engineering and Metal Technology, P. O. Box 6235, 5600 HE Eindhoven, The Netherlands

<sup>2</sup>Dutch Polymer Institute, P. O. Box 902, 5600 AX Eindhoven, The Netherlands

Received 2 June 2003; accepted 26 October 2003

**ABSTRACT:** The friction and abrasive wear of blends of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were measured. The coefficient of friction decreases only slightly with an increasing PPO fraction, while the abrasive wear decreases largely upon the introduction of increasing amounts of PPO. It is clearly shown that the abrasive wear resistance of the PS/PPO blends increases with an increasing strain hardening modulus of the blend.

The wear rate change between 20 and 40 wt % PPO is ascribed to a transition in the failure mechanism from predominantly brittle to predominantly tough. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2689–2692, 2004

**Key words:** blends; PS/PPO; polystyrene; poly(2,6-dimethyl-1,4-phenylene oxide); strain-hardening; wear resistance; tribology; friction; entanglements

## INTRODUCTION

Polymer wear and friction play an important role in a range of mechanical components such as gears, cams, wheels, brakes, seals, conveyors, and bearings. Furthermore, polymers can be found in the field of piping, pumps, chute lines, and conveyer aids where wear resistance is the main issue. Although polymers have been used for over 40 years, knowledge on their behavior in sliding contact is still largely empirical in nature. A proper understanding is necessary for control and prediction of polymer performance. A vast amount of literature has appeared over the years in which relations between tribological performance and polymer properties are described in terms of mechanical parameters, such as yield and shear stress, toughness (as defined by the product of stress- and strain-to-break), plasticity index, Youngs' modulus, and hardness.<sup>1–4</sup> These studies and reviews proved their value in predicting polymer behavior in sliding wear and friction to a certain level. However, the validity of the correlations under all circumstances can be questioned, as, for example, the values of stress- and strain-to-break are strongly influenced by experimental parameters, such as temperature and strain rate.<sup>5–7</sup> Furthermore, the yield stress is strongly influenced by the thermomechanical history of the polymer in question.<sup>5,8</sup>

All of the mechanical parameters mentioned above, which are normally obtained in tensile testing, are mainly the result of the primary and secondary interactions between polymer chains. Primary interactions find their origin in the polymer network and include entanglements, strain hardening, and chain slippage. Secondary interactions originate from interactions between polymer chains, as ruled by van der Waals forces and dipoles. Both primary and secondary interactions find their origin in the specific structure of the polymer backbone and the presence and length of side-chains.<sup>5,9,10</sup> In this light, polymer behavior and, more specifically, polymer wear should be addressed in terms of these primary and secondary interactions. Thus, in terms of strain softening, strain hardening, and entanglement density, as these parameters are directly related to polymer structure and interactions between polymer chains.<sup>5,8,11,12</sup>

To show the importance of strain hardening and entanglement density on the abrasive wear of polymers, a series of polystyrene (PS) blended with poly(2,6-dimethyl-1,4-phenylene-oxide) (PPO) was measured on a pin-on-disk apparatus. A P600 SiC sandpaper was used as a counter surface. Abrasive wear and friction were measured as a function of the PPO content. PS and PPO are miscible on a molecular level and form a compatible mixture; this results in a single glass-to-rubber transition temperature.<sup>11,12</sup> Recent research showed that the strain softening of the PS/PPO composite decreases and the strain hardening increases with increasing PPO content.<sup>11,12</sup> Furthermore, it was shown that the network density increases almost linearly with the fraction PPO. Similar effects

Correspondence to: Y. J. Mergler (y.j.mergler@ind.tno.nl).

TABLE I  
Rubber-Plateau Modulus, Strain Hardening Modulus,  
 $E$  Modulus, and Glass Transition Temperature of the  
PS/PPO Blends, According to van Melick<sup>11,12</sup>

PS/PPO	$G_N^o$ (MPa)	$G_r$ (MPa)	$E$ (MPa)	$T_g$ (K)	$M_e$ (g/mol)
100/0	0.16	13	3,300	378	18,700*
80/20	0.26	25	3,000	391	11,400
60/40	0.49	48	2,700	410	8,200
40/60	0.57	58	—	427	6,400
20/80	0.66	65	—	449	5,300

$M_e$  values were calculated according to Prest and Porter<sup>14</sup> with the exception of pure PS, which was obtained from Wu<sup>9</sup> (see Results and Discussion).

were seen when PS was crosslinked during polymerization,<sup>11,12</sup> showing the importance of the polymer network on the strain hardening and softening behavior.

## EXPERIMENTAL

The wear and friction measurements were performed on PS/PPO blends. The materials were taken from the same batches as used by van Melick et al.<sup>11,12</sup> The materials tested contained 0, 20, 40, 60, and 80% PPO, respectively. To obtain polymer sheets, the granular material was compression molded.<sup>11,12</sup> All materials were preheated in a mold of  $60 \times 60 \text{ mm}^2$  at  $80^\circ\text{C}$  above their respective glass transition temperatures, as shown in Table I, for 15 min and subsequently pressed in five steps of increasing force, up to 300 kN, during 5 min. In between the steps, the pressure was released to allow for degassing. The mold was cooled to room temperature in a cold press under a pressure of 100 kN. Samples were then cut from the sheets with final dimensions of  $5 \times 5 \times 4 \text{ mm}^3$ .

Values of the rubber-elastic modulus, strain hardening,  $E$  modulus, and  $T_g$  are taken from the work of van Melick et al.<sup>11,12</sup> and are displayed in Table I. The hardness was measured with a Shore durometer. As an indenting body, a steel pencil is used in the form of a rounded cone, revealing a Shore D hardness value of  $86 \pm 1$  for all samples.

Abrasive wear and friction were measured on a pin-on-disk apparatus<sup>13</sup> with P600 SiC sandpaper as a counter surface. The polymer pin slid over the sandpaper with a constant sliding speed of 0.01 m/s. The applied normal force was 5N. The polymer pin slid spiralwise from the outside of the disk toward the inside, thereby continuously meeting a fresh abrasive surface. The sliding distance was about 10 m. The wear factor,  $k$ , is expressed here as the weight loss per sliding distance per normal load. The displayed friction and wear values are an average of three experiments.

## RESULTS AND DISCUSSION

### Strain hardening

The values of the rubber-plateau modulus,  $G_N^o$ , as a function of the PPO fraction, as measured by van Melick,<sup>11,12</sup> are shown in Table I. From the rubber-elastic theory, it is known that the modulus relates to the molecular weight between entanglements,  $M_e$ , by:

$$G_N^o = \rho_r RT / M_e \quad (1)$$

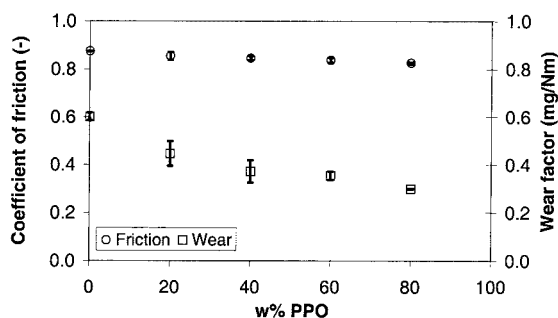
In which  $\rho_r$  is the density of the polymer in the rubbery state,  $R$  is the molar gas constant, and  $T$  is the absolute temperature.  $M_e$  is inversely related to the network density,  $\nu_e$ , by

$$M_e = \rho_g N_A / \nu_e \quad (2)$$

with  $\rho_g$  the density in the glassy state and  $N_A$  Avogadro's number.

The rubber-plateau modulus depends on the presence of chemical and physical crosslinks between polymer chains. The value of the rubber plateau modulus is a measure of the elasticity of a polymer melt above its softening temperature. It is thus possible for a thermoplastic to exhibit rubber-like properties, in the absence of chemical crosslinks, due to the presence of (physical) entanglements between polymer chains. The strain hardening modulus,  $G_r$ , is also a measure for the configurational restrictions and intermolecular interactions of polymer chains under a constant strain rate at high strain levels. It can serve as a measure of the (physical) entanglements present under the conditions of (mechanical) testing. The strain hardening modulus can be determined from uniaxial compression curves at large strains<sup>10-12</sup> and is, similar to  $G_N^o$ , a function of the network density.

The strain hardening modulus and the rubber-elastic modulus both show an increase with increasing PPO fraction, as can be seen in Table I. However, the absolute values of  $G_N^o$  and  $G_r$  are different as the rubber-plateau modulus is measured in the rubber-elastic region at high temperatures, where the polymer chains have full mobility and where the properties are determined by the entangled network. The strain hardening modulus is determined upon plastic deformation of the polymer, where no full chain mobility is encountered. Haward<sup>10</sup> found similar trends in  $G_N^o$  and  $G_r$ , upon viewing a range of (semicrystalline) polymers. However, there are a few points that need further attention. First of all, both authors show that  $G_r$  decreases with increasing temperature, which is unexpected if eq. (1) is considered. Van Melick<sup>11,12</sup> assumed that relaxation can overrule the entropic character of the polymer network, leading to a decrease of the strain hardening modulus with an in-



**Figure 1** Coefficient of friction and the wear factor as function of the PPO fraction of the PS/PPO blends.

creasing temperature. Furthermore, there is a marked difference in absolute values of  $G_N^o$  and  $G_r$ . Haward<sup>10</sup> concluded that an additional “frictional” factor should be present in  $G_r$ , compared to  $G_N^o$ , which determines the efficiency of the entanglements. It is quite likely that Van der Waals forces between polymer chain segments contribute to this additional factor, making the chain segments between entanglements less mobile.

Prest and Porter<sup>14</sup> showed that the  $M_e$  for PS/PPO blends depends solely on the  $M_e$  of PS and the fraction of PPO present in the blend. The molecular weight between entanglements of the blend is calculated according to the method given by Prest and Porter<sup>14</sup> and is shown in Table I.  $M_e$  decreases with an increasing PPO fraction. This implies that the network density increases with increasing PPO fraction, which is confirmed by the work of van Melick et al.<sup>11,12</sup>

### Wear and friction

The coefficient of friction of the PS/PPO blends and the abrasive wear factor is shown in Figure 1 as a function of the PPO fraction. The coefficient of friction decreased slightly with increasing PPO content, while the wear factor showed a twofold decrease from PS/PPO 100/0 to PS/PPO 20/80.

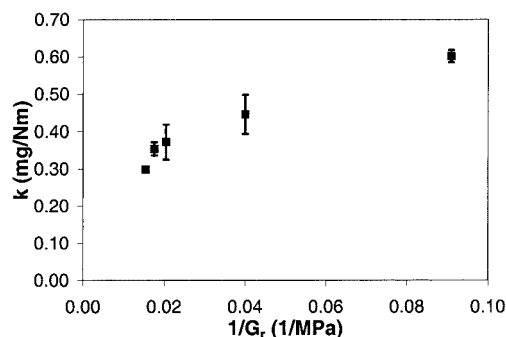
Recently, Tervoort et al.<sup>15</sup> and Visjager<sup>16</sup> showed that the wear resistance of polyethylene increases with an increasing number of entanglements per chain. As shown above, the network density,  $M_e$ , and the strain hardening modulus are all interrelated.<sup>11,12</sup> An increase in the number of entanglements per chain, either by increasing the molecular weight (in case of polyethylene<sup>16</sup>) or by decreasing the molecular weight between entanglements (in case of the PS/PPO blends) should result in an increased wear resistance. This was confirmed by our experiments, as shown in Figure 2. The abrasive wear factor,  $k$ , expressed in mg/Nm, is shown as function of the inverse of the strain hardening modulus. It can be seen that wear increases with a decreasing strain hardening modulus

or, with a decreasing network density, as  $G_r$  and  $\nu_e$  are related.

By increasing the PPO fraction of the blend, several mechanical properties change (see Table I and van Melick<sup>11,12</sup>). The strain hardening modulus rises and the strain softening decreases, while the yield stress remains largely unaffected<sup>11,12</sup> with an increasing PPO concentration. The yield stress and strain softening behavior are mainly determined by secondary interactions between polymer chains.<sup>5</sup> The fact that a higher network density results in a reduced stress drop in tensile or compressive testing is attributed to the stabilizing contribution of the polymer network at small strains.<sup>5,11,12</sup> This behavior is also very likely to be responsible for the results on the Shore D hardness values. Apparently, there is a competition between the expected decreasing hardness values due to the decreasing Young’s modulus<sup>6</sup> and the expected increasing hardness values due to the increase in the strain hardening modulus, both with increasing PPO fraction.

In the failure behavior of polymers, strain softening and strain hardening play an important role. Strain softening induces localization of strain, while strain hardening can stabilize the evolution of the localized plastic zone, provided that the ratio between the yield stress and the strain hardening modulus is small enough.<sup>17</sup> Whether a polymer shows brittle or ductile behavior strongly depends on its reaction to strain localization and on the stabilizing effect of strain hardening at small strains.<sup>11,12</sup> If the exerted strain can be evenly distributed over the polymer chains, the material behavior is tough. If not, brittle failure will occur.

Yang et al.<sup>18</sup> also studied the wear and friction of PS/PPO blends with, among other techniques, a Taber abrasion test. Yang et al.<sup>18</sup> found a sudden decrease in the macroscopically measured wear rate at around a PPO fraction of 30 to 40 wt %, at a normal load of 25 or 60N, respectively. The sudden decrease in the wear rate with PPO weight fraction was ascribed to a change in the main deformation mechanism from predominantly crazing to shear yielding.<sup>18</sup> Wu<sup>9</sup> showed



**Figure 2** The abrasive wear factor,  $k$ , as function of the inverse of the strain hardening modulus,  $G_r$ .

that the molecular aspects of craze or yield behavior are controlled by two chain parameters: entanglement density and characteristic ratio. According to Wu's classification,<sup>9</sup> a shift of predominantly crazing to predominantly shearing can be expected for PS/PPO with PPO concentrations larger than 25 wt %. The change in the wear factor with an increasing strain hardening modulus, which we found (Figs. 1 and 2), should be ascribed to a change in the failure mechanism from brittle to tough.

It should be mentioned here that the same principal objections in using stress-strain curves to obtain material parameters also accounts for the strain hardening modulus. The strain hardening modulus will be influenced by temperature and strain rate.<sup>11,12</sup> The reason we choose to display the wear factor as function of the strain hardening modulus is that it is relatively easily to measure the strain hardening modulus in compressive tests. Furthermore, although the absolute values are different, the rubber-plateau modulus and the strain hardening modulus showed the same trend with increasing PPO fraction. As all our blends are measured under similar conditions, the strain hardening modulus can be used to relate with the wear behavior within this series of PS/PPO blends.

### CONCLUSION

The wear and friction of PS and blends of PS with PPO were studied and related to the strain hardening behavior of the blends in compressive testing. It was found that

1. with an increasing PPO fraction the coefficient of friction slightly decreases and the wear factor,  $k$ , expressed in mg/Nm, largely decreases;
2. the strain hardening modulus behaves in a similar manner as the rubber-plateau modulus for the PS/PPO blends and can be used as a measure of the wear resistance of the PS/PPO blends;
3. the wear resistance is governed by the ability of the polymer chains to distribute the exerted

forces evenly and increases with an increasing number of entanglements per chain or an increasing network density;

4. the wear rate changes between 20 and 40 wt % PPO, which was ascribed to a change in the failure mechanism from predominantly brittle to predominantly tough.

Dr. L. E. Govaert of the Eindhoven University of Technology is gratefully acknowledged for providing the materials. The authors also acknowledge Ir. C. J. M. Meesters and ing. J. G. H. van Griensven of the Eindhoven University of Technology for the use of their pin-on-disk apparatus.

### References

1. Steijn, R. P. In *Failure of Plastics*; Brostow, W.; Corneliusen, R. D., Eds.; Hanser Publishers: Munich, 1986; Chap. 19.
2. Briscoe, B. J. In *Composite Materials Series, Vol. 1, Friction and Wear of Polymer Composites*; Friedrich, K., Ed.; Elsevier: Amsterdam, 1986; Chap. 2.
3. Ratner, S. B.; Farberova, I. I. In *Abrasion of Rubber*; James, D. I. Ed.; MacLaren and Sons: London, 1967.
4. Lancaster, J. K. *Wear* 1969, 14, 223-239.
5. Meijer, H. E. H.; Govaert, L. E.; Smit, R. J. M. *ACS SympSer* 2000, 759, 50-70.
6. Van Krevelen, D. W. In *Properties of Polymers*; Elsevier, Amsterdam, 1997; 3<sup>rd</sup> ed..
7. Tervoort, T. A. Ph.D. Dissertation. Eindhoven University of Technology, The Netherlands, 1996.
8. Govaert, L. E.; van Melick, H. G. H.; Meijer, H. E. H. *Polymer* 2001, 42, 1271-1274.
9. Wu, S. *Polym Eng Sci* 1990, 30, 753-761.
10. Haward, R. N. *Macromolecules* 1993, 26, 5860-5869.
11. van Melick, H. G. H.; Govaert, L. E.; Meijer, H. E. H. *Polymer* 2003, 44, 2493-2502.
12. van Melick, H. G. H.; Bressers, O. F. J. T.; den Toonder, J. M. J.; Govaert, L. E.; Meijer, H. E. H. *Polymer* 2003, 44, 2481-2491.
13. Mark, H. F., Ed. *Encyclopedia of Polymer Science and Engineering*, Vol. 1; Wiley: New York, 1985, pp. 1-35.
14. Prest, W. M.; Porter, R. S.; *Polym Sci Eng, Part A* 1972, 10, 1639.
15. Tervoort, T. A.; Visjager, J.; Smith, P.; *Macromolecules* 2002, 35, 8467.
16. Visjager, J. Ph.D. Dissertation; ETH Zurich, No. 13978 (Available via [www.eth.ch](http://www.eth.ch)).
17. Schrauwen, B. A. G. Ph.D. Dissertation; Eindhoven University of Technology, The Netherlands, 2003 and Schrauwen, B. A. G.; Govaert L. E.; Haward, R. N. *Polymer* 1987, 28, 1485.
18. Yang, A. C. M.; Wu, T. W. *J Polym Sci B: Polym Phys* 1997, 35, 1295-1309.