Connection between dynamic mechanical properties and sliding wear resistance of polymers

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The viscoelasticity of several polymers has been determined using dynamic mechanical analysis (DMA). For the same materials the sliding wear in multiple scratching along the same groove has also been determined. The materials studied were polycarbonate (PC), polystyrene (PS), styrene/acrylonitrile (SAN), Surlyn, polyethersulfone (PES), acrylonitrile/butadiene/styrene (ABS), polypropylene (PP), polytetrafluoroethylene (PTFE), low density polypropylene (LDPE) and Santoprene (an elastomer). Sliding wear was determined for several constant loads between 5 and 15 N. The penetration depth R_p and the residual depth R_h obtained from wear tests were confronted with DMA parameters: E', E'' and $\tan \delta$. An evident correlation between $\tan \delta$ and R_p is seen. Both penetration depth and residual depth increase along with $\tan \delta$. Surface roughness obtained from atomic force microscopy (AFM) provides another kind of useful tribological information, with the highest value obtained for PS.

Introduction

Tribological properties, especially wear resistance, are important not only for technology but also for economic reasons. An eloquent argument for the economic importance of tribology has been provided by Rabinowicz.[1] Ignorance of tribological phenomena and insufficiency of coherent programmes of education and research to remedy this situation cause a tremendous waste of resources. Moreover, the ongoing replacement of metal parts by polymeric ones behooves to better understanding of polymer tribology. A review of polymer tribology and the issues involved has been published.[2] In general, polymer tribology is much more difficult than that of metals.

There are several research groups working on polymer tribology, including teams of Briscoe and his colleagues,[3–8] Friedrich with co-workers[9] and Dasari et al.[10] However, the basic understanding of polymer tribology is still insufficient. For example, numerous attempts to connect hardness to wear have been made. The results are either not meaningful or even contradicted by other results.

The approach taken consists in the determination of sliding wear by multiple scratch tests.[11–14] A scratch test method involves scratching the surface of samples and measuring the depth of the groove while the scratch is being made. This can be carried out under either a constant load, or a progressively increasing load, or else under a stepwise increasing load. The resulting values are called the penetration depths and represented by the symbol R_p. It has been found that the depth recovers or heals after scratch, with the bottom of the groove going up and settling at a final level called the residual depth R_h.[11–16] This could be explained by the inherent viscoelasticity of polymers.[17–22] From this point of view, these two parameters R_p and R_h determined from the scratch tests could have a correlation with the dynamic mechanical properties.

Dynamic mechanical analysis (DMA) is classified as a part of mechanics and constitutes a well known method to characterize the viscoelasticity of materials. There is a book and book chapter devoted to this technique.[19,20] The most often used property is

$$\tan \delta = E''/E' \tag{1}$$

determined as a function of either temperature or frequency of sinusoidal load imposition. Here E' is the storage modulus representing elastic (solid-like) behavior while E'' is the loss modulus representing viscous flow (liquid-like) behavior.

Thus, an objective of the present study is to investigate the existence of a connection between dynamic mechanical properties such as $\tan \delta$ and scratch or wear resistance of polymers in terms of R_h and R_p. Moreover, the authors have decided to investigate the scratch topography using atomic force microscopy (AFM) of polymeric materials – also looking for a possible connection to R_h and R_p.

Experimental

Materials

Materials selected were based on ranges of their mechanical properties and a variety of applications.

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1 Penetration depth R_p as function tan δ measured at room temperature
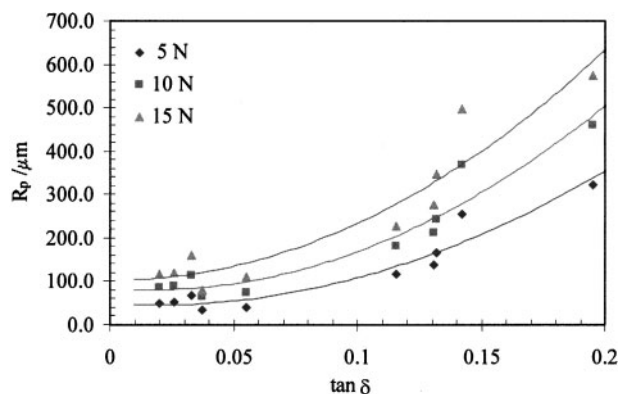
2 Residual depth R_h as function of tan δ measured at room temperature

Polystyrene (PS) was purchased from Aldrich Chemicals Company. Styrene/acrylonitrile (SAN, Luran) was supplied by BASF, Ludwigshafen/Rhein, Germany. Santoprene was supplied by Advanced Elastomer Systems, Houston, TX. Santoprene is a thermoplastic elastomer – it contains ethylene propylene diene mono-mer (EPDM) and polypropylene (PP) copolymer. Surlyn 8140 was supplied by E. I. du Pont de Nemours, Wilmington, DE., which is a thermoplastic resin, an advanced ethylene/methacrylic acid (E/MAA) copoly-mer, in which the MAA acid groups have been partially neutralized with sodium ions. Polycarbonate (PC), acrylonitrile/butadiene/styrene (ABS) and polytetra-fluoroethylene (PTFE) were supplied by the Dow Chemical Company. Polypropylene (PP) was supplied by Phillips. Low density polyethylene (LDPE) was supplied by Huntsman. Polyethersulphone (PES) was supplied by Solvay Engineered Plastics.

Sliding wear testing

A microscratch tester (MST) from CSEM Instruments in a multiple scratch mode has been used. The procedure and instrument used was described in detail before elsewhere.[2,11–15,23] Fifteen scratches along the same original groove were performed for each constant load; 5·0, 10·0 and 15·0 N at the room temperature (25°C). The scratch speed was 5 mm min^{-1}. The scratch length was 5·0 mm. However, for detailed analysis, the depth at the middle of the range (2·5 mm) has been used. The accuracy of the depth determination was ±7·5 nm.

Dynamic mechanical analysis (DMA)

The tests were carried out using DMA7e apparatus from Perkin Elmer Co. Specimens were analyzed in rectan-gular form (approximately $20·0 \times 6·0 \times 3·0$ mm) using three point bending fixture in the temperature scan mode. The frequency used was 1·0 Hz.

Atomic force microscope (AFM)

The AFM used was a Quesant Instrument Corporation Q-Scope in the wave mode. It has provided values of the roughness along the scratching grooves.

Sliding wear resistance and DMA

As discovered earlier, for many polymers the consecu-tive scratch tests produce gradually diminishing deepen-ing of the groove, leading to an asymptotic depth that does not change with the number of the scratches.[13] Thus, sliding wear can be determined quantitatively
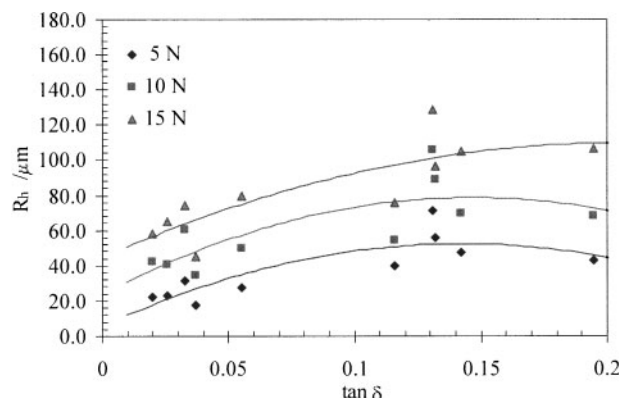
from a multiple scratch test as

$$W(F) = \lim_{n \to \infty} R_h(F) \qquad (2)$$

where $W(F)$ is the wear for a given indenter geometry, force F and temperature T while n is the number of scratch tests.[13] It is found that 10–15 multiple scratch tests seem to be sufficient. Thus, the depth at the fifteenth test has been used as a measure of sliding wear.

It has been assumed that viscoelasticity should manifest itself in both mechanics and tribological proper-ties of polymeric materials. Therefore the authors try to make the connection between dynamic mechanical parameters, namely E', E'', tan δ and sliding wear resis-tance, namely asymptotic R_p and R_h values. A clear correlation of tribological parameters with tan δ is found.

Figure 1 shows a plot of the penetration depth versus tan δ at room temperature (25°C). The penetration depth R_p increases parabolically with tan δ; it is found as follows

$$R_p(\mu m) = 9222·8\tan^2\delta - 311·19\tan \delta + 47·27$$

at the load of 5 N $\qquad (3a)$

$$R_p(\mu m) = 12533·0\tan^2\delta - 405·3\tan \delta + 83·65$$

at the load of 10 N $\qquad (3b)$

$$R_p(\mu m) = 13389·0\tan^2\delta - 28·86\tan \delta + 102·79$$

at the load of 15 N $\qquad (3c)$

As expected, the R_p decreases with decreasing load. These are plausible results. The more a polymer is liquidlike, the easier it should be to penetrate the surface and create a deeper scratch or wear. Moreover, it is seen that the curves show clearly the same trend at different loads.
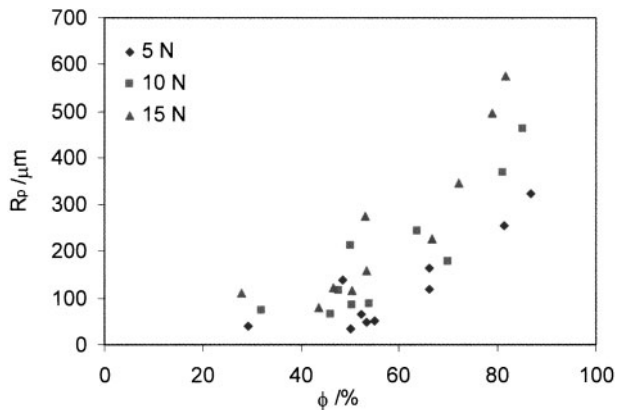
A similar result is found in a plot of residual depth R_h versus tan δ at room temperature, as shown in Fig. 2. The parabolic connection between R_h and tan δ can be represented by the following equations

$$R_h(\mu m) = -2326\tan^2\delta + 659·55\tan \delta + 5·59$$

at the load of 5 N $\qquad (4a)$

$$R_h(\mu m) = -2580·4\tan^2\delta + 753·22\tan \delta + 23·69$$

at the load of 10 N $\qquad (4b)$

3 Penetration depth R_p as function of percentage recovery ϕ measured at room temperature

4 Residual depth R_h as function of percentage recovery ϕ measured at room temperature

$$R_h(\mu m) = -1539{\cdot}6\tan^2\delta + 632{\cdot}75\tan\delta + 44{\cdot}71$$

at the load of 15 N (4c)

From Fig. 2 it is found that at low tan δ, R_h increases gradually with tan δ and it tends to decrease at higher tan δ. A similar explanation as discussed above is applicable only for low tan δ. We need to consider the results for higher tan δ values somewhat more in detail.

As also discussed above, the higher the tan δ is, the more polymers are liquid-like. At least two possible phenomena need to be considered for viscous liquid-like polymers. One is that the liquid-like behavior facilitates the possibility of a material to be moved away from its original location. Consequences of this are seen in Fig. 2 at low tan δ and obviously in Fig. 1 at all ranges of tan δ. Another aspect is: liquidlike behavior also facilitates the healing. As also seen in Fig. 2, the R_h tends to decrease as increasing tan δ at a very high value of tan δ. There is still an entrenched opinion that restoring the original shape is characteristic for elastic solidlike materials. This explanation needs more clarification. A basic phenomenon that can be observed when removing a load imposed upon the liquid in a container needs to be recalled. The liquid recovers its size and shape when a load is removed. Thus, the authors propose that at a very high tan δ, the healing due to viscous liquid-like behavior can be observed; it competes with deeper scratches which go symbatically with liquid-like behavior as well.

In order to know more about the healing phenomena occurring during sliding wear tests, R_h and R_p are plotted as a function of percentage recovery ϕ defined in as

$$\phi = \left(1 - \frac{R_h}{R_p}\right) \times 100\%$$ (5)

shown in Figs. 3 and 4. It is found from Fig. 3 that the penetration depth R_p tends to increase with percent recovery ϕ. This tendency is consistent with the plot of R_p as a function of tan δ. The result seems to confirm the explanation that the recovery during sliding wear test might come from the viscous flow constituent of viscoelasticity. At the same time, the residual depth R_h versus percentage recovery ϕ does not show such a clear tendency.
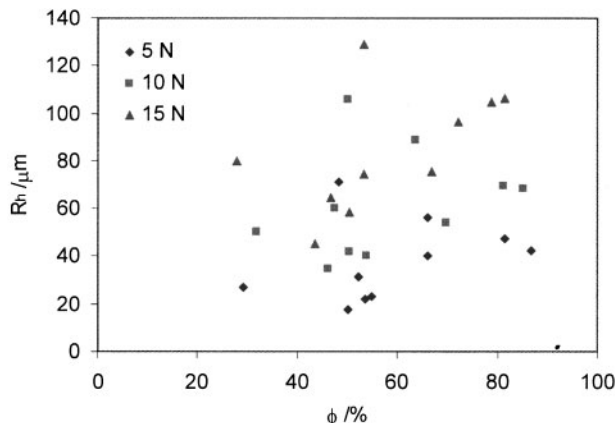
Figure 5 shows a plot of percentage recovery ϕ as function of tan δ. At small values of tan δ it is found that ϕ gradually decreases with increasing tan δ, then the tendency changes fairly abruptly; ϕ increases with tan δ for tan δ larger than $\sim 0{\cdot}1$. This result strengthens the authors explanation formulated above. At very low tan δ, the healing also occurs but due to the elastic solid-like recovery of the polymer; this effect tends to decrease as tan δ increases. At intermediate tan δ values neither solid-like recovery nor liquid-like flow helps in healing. However, at higher tan δ the recovery due to the viscous liquid-like behavior is dominant and helps – just as solid-like behavior helped in the left end of the diagram in Fig. 5. The higher the tan δ is, the more percentage recovery seen in the right part of the diagram.

Various kinds of polymers: PC, PS, PP, LDPE, PES, PTFE, Santoprene, Surlyn and SAN have been investigated. One might argue that the molecular mass effect also plays a role in scratch or wear resistance, as shown in the case of adhesion and friction by Chen et al.[24] They declared that the population of the chain ends at the surfaces was the most important factor that determined the adhesion, adhesion hysteresis, friction and wear between two polymer surfaces. While it would be difficult to have molecular masses of different polymers coming from different sources to be exactly the same, we use the polymers with molecular weights which are quite high. Thus, the concentration of chain ends can be
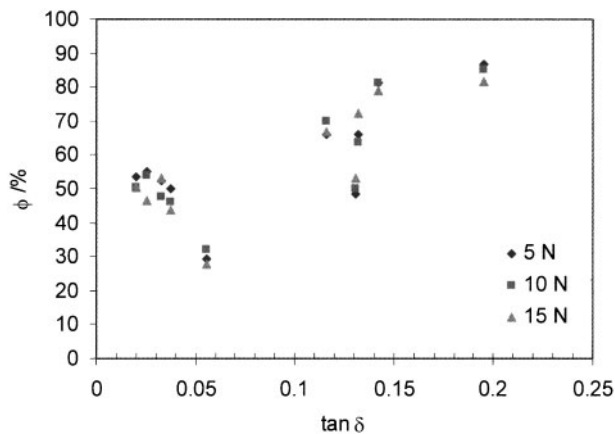
5 Percentage recovery ϕ as function of tan δ measured at room temperature

Table 1   Wear resistance and dynamic mechanical parameters of some polymeric materials at room temperature

Polymeric materials	R_p, μm			R_h, μm			tan δ
	5 N	10 N	15 N	5 N	10 N	15 N	
PC	47·9	84·6	117·6	22·3	42·0	58·2	0·0199
PP	165·2	243·5	347·0	56·0	88·6	96·5	0·1320
PS	38·4	73·4	110·8	27·2	50·0	80·0	0·0554
PTFE	137·8	212·1	275·9	71·1	105·9	129·0	0·1308
SAN	35·2	64·2	80·1	17·6	34·6	45·2	0·0372
Santoprene	253·7	368·0	496·4	47·3	69·4	104·7	0·1420
ABS	66·1	114·8	159·2	31·5	60·2	74·4	0·0328
Surlyn	118·0	179·8	227·0	40·0	54·2	75·5	0·1157
PES	50·9	87·6	121·2	23·0	40·4	64·8	0·0257
LDPE	322·7	461·1	575·4	42·6	68·5	106·3	0·1949

assumed low enough so that effects arising from the chain end concentration differences can be neglected. The values of R_p and R_h from the fifteenth scratch and the tan δ values of the respective polymer at room temperature are shown in Table 1.

Sliding wear resistance and scratch topography

It is assumed that AFM is a good technique for evaluation of surface of materials after scratch and wear testing; one of the interesting parameters obtained from AFM, namely average surface roughness R_a is the average deviation from the mean surface plane. In general, surface roughness has a simple relation with scratch visibility.[10] A material showing low surface roughness would show low scratch visibility. Table 2 shows the average surface roughness R_a of selected polymers for 10 μm scan size and 1 Hz scan rate after 15 sliding wear tests performed at the applied load of 15·0 N. PS has an average surface roughness $R_a =$ 55·22 nm while PC has 13·95 nm. Thus, there is a large difference in surface roughness of these two polymers even though their R_p values listed in Table 1 are comparable while the R_h values for PS are only some 20% higher than those for PC.

The difference in behavior between PS and PC deserves a further discussion. Narisawa shows that the fracture toughness of PS is only about one third of the value for PC, 1·00–1·29 versus 3·60 MPa m$^{1/2}$ (Ref. 25). The authors also need to remember crazing, a frequent mechanism of polymer responses to deformation, thoroughly discussed by Donald.[26] When crazing occurs, it drastically increases the ability of the surface to scatter light with the consequent increase in scratch visibility. It is recalled further that the surface roughness depends not only on the inherent characteristics of the materials but also on the sample preparation procedure. It is concluded that the roughness from AFM is useful

tribological parameter additional to friction, scratch and wear testing. The authors would like investigate connections between DMA results, scratching and sliding wear tests, and AFM results further. The authors note papers by McGuiggan and co-workers on friction from AFM experiments and an even more pertinent paper on tan δ determination from AFM.[27,28] The authors would like to return to these issues in future papers.

It is noted that the highest surface roughness value in Table 2 is that for PS. This result might be connected to recent work on brittleness. According to a definition of brittleness, PS has by far the highest value of brittleness among a variety of polymers.[29] A definition of brittleness was needed since the concept was used previously as a qualitative one.[30,31]

Concluding remarks

A connection between dynamic mechanical properties and scratch/wear resistance has been demonstrated. When plotting tan δ as a function of penetration depth or residual depth, a parabolic dependence is observed. However, a clear connection with other DMA parameters E' and E'' has not been found. One possible reason is that tan δ is independent of sample geometry while the other two parameters are geometry dependent. The average surface roughness R_a obtained from AFM provides us with information about visibility. Comparing these materials, it is found that PS has the highest sliding wear groove visibility even though its R_p and R_h values are comparable to those of PC.

In the beginning the need for improved understanding of polymer tribology has been noted. Another useful technique of surface evaluation is the nanoindentation creep which can be connected to glass transition temperatures of polymers.[32–35]

Table 2   Average surface roughness R_a of some polymeric materials after 15 scratch tests performed at applied load of 15 N

Materials	R_a, nm
PC	13·95
Surlyn	28·10
PES	28·33
PP	48·08
PS	55·22

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