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Characterization of orientation in polyethylene by scratch testing

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Abstract: Microscratch experiments were performed to evaluate effects of uniaxial stretching by 200 % in low density polyethylene (LDPE) along parallel and perpendicular directions with respect to stretching. Penetration depth, healing depth and viscoelastic recovery have been determined. Clear orientation effects are seen. The direction parallel to the extension axis shows strong resistance to scratching and also the highest recovery (a memory effect). Unoriented material exhibits behavior intermediate between that of oriented samples in parallel and perpendicular directions. The sliding wear was determined by multiple scratching along the same groove and here also was found orientation dependence. Polarized micro-Raman experiments on the oriented LDPE samples were carried out. Since scratching and sliding wear results are strongly affected by polymer orientation, one can use both kinds of tests as a measure of orientation – and also to vary orientation to control tribological properties.

Keywords: polymer orientation, sliding wear, brittleness, polarized micro-Raman

Introduction

Surface wear phenomena are fairly well understood for metals [1]. More understanding is needed for polymer-based materials (PBMs) although certain experimental [2, 3] as well as computational [4, 5] progress has been achieved.

Within the field of PBMs tribology, relatively much attention has been devoted to friction. This is in spite of the fact that friction values *per se* do not represent wear of the material. Wear can be determined in a variety of ways. In our experience pertinent information is obtained from scratch testing [6, 7] and also by sliding wear determination that consists of multiple scratching along the same groove [8 - 11]. One determines the penetration (instantaneous) depth R_p and the recovery (after healing) depth R_h. From these two values the percentage recovery can be calculated as:

$$f = \frac{R_p - R_h}{R_p} 100\% \quad . \tag{1}$$

We note that in service (and also in transport before service) surface damage by scratching can occur repetitively - leading to wear.

One of our results is the discovery of strain hardening in sliding wear [8]. After several scratches along the same groove, the recovery depth exhibits asymptotic behavior. In other words, further scratches have no effect on the depth. Such asymptotic values when they appear provide a reliable way for comparison of wear characteristics in different polymer systems. Moreover, brittleness has been defined [11] as:

$$B = \frac{1}{\varepsilon_b E'} \tag{2}$$

Here ε_b = elongation at break in tensile testing while E' is the storage modulus determined in dynamic mechanical testing (DMA) [12] at 1.0 Hz. A one-to-one relationship between the viscoelastic recovery f and brittleness B, both pertaining to the same temperature, has been demonstrated [11].

Properties of PBMs are strongly dependent on orientation [13 - 16]. Orientation effects on abrasive wear in polymers were studied by Cayer-Barrioz and co-workers [17]. For polypropylene (PP) there is a large body of evidence from the group of Karger-Kocsis [18 - 20] as well as others [21 - 23] demonstrating the effects of molecular orientation on mechanical properties. In particular, for polyethylene strong effects of orientation have been reported already in 1995 [24]. Environmental stress cracking in high density polyethylene (HDPE) [25] and a combination of photodegradation and stress cracking in polystyrene (PS) [26] have been related to orientation. Hashimoto and coworkers have reported anisotropy of optical absorption in oriented ultra thin low density polyethylene (LDPE) films [27].

Still further, wear mechanism of polyethylene under biomechanics motions in human orthopedic implants is not well understood. However, a simulation in wear bench tests of interactions between the molecular structure of ultrahigh molecular weight PE (UHMWPE) and a multi-directional stress field experienced on the articulated surfaces of artificial joints (similar to hip and knee joint motion in the human body) shows that unidirectional sliding produces the least amount of wear, reciprocating motion increases wear significantly, while cross-shear motion produces the highest amount of wear [28, 29].

Given these results, it seemed worthwhile to evaluate effects of orientation on scratching behavior. The most widely used polymer, namely LDPE, has been chosen as the object. LDPE is a semicrystalline polymer whose crystalline sections consist of lamellar crystallites (orthorhombic) randomly oriented in an amorphous matrix. It is well known that mechanical deformation, for instance in tension or else during injection, results in orientations of crystallites parallel to the tensile direction [30 - 33] and to a lesser degree in orientation of the amorphous regions. Several experimental techniques have been developed to identify molecular orientation in polymers [34 - 40]. In our work microscratch testing and Raman spectroscopy have been used to investigate orientation in LDPE. The results are reported below.

Results and discussion

MicroRaman results

Figure 1(a-c) shows the Raman spectra corresponding to unoriented, parallel and perpendicular directions of the polymer in the range 1000-1500 cm^{-1}. We see significantly anisotropic spectra for oriented samples, with high intensity signals for the parallel-to-orientation direction and low intensities for the perpendicular direction. Unoriented samples have somewhat lower intensities than the intensities for the parallel direction. The 1424-1460 cm^{-1} range corresponds to the Fermi resonance and overtones. Raman lines which appear in the region of 1067-1301 cm^{-1} arise from vibrations of the –C-C- backbone: 1301 (-CH_2- twisting), 1133 (symmetric stretching C-C) and 1067 cm^{-1} (asymmetric stretching C-C).

LDPE has a significant number of short chain branches - including ethyl and butyl groups. The presence of those branches is evidenced by the methyl groups vibrations peak at 1374 cm^{-1}. The Raman spectra in Figure 1 show that the stretched LDPE subjected to scratch testing is an oriented polymer.

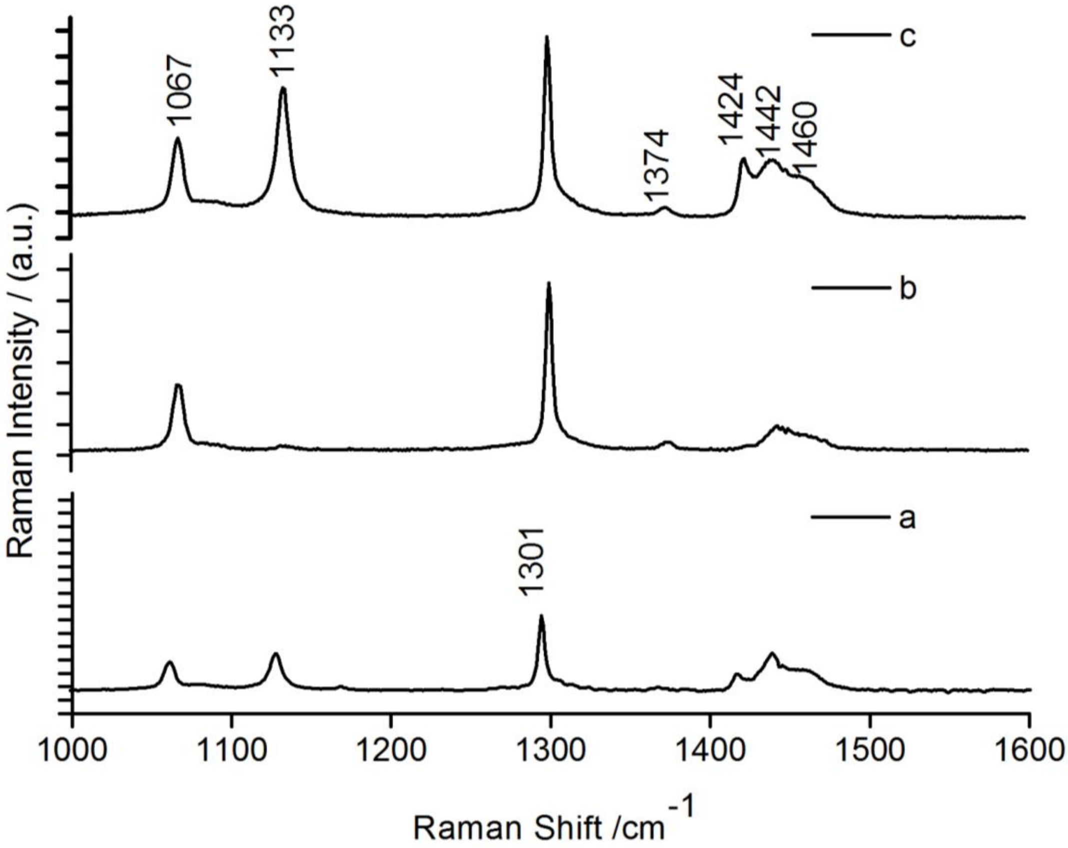

Fig. 1. Raman spectra for LDPE: a) unoriented sample; b) and c): polarization plane parallel and perpendicular to the stretching direction, respectively.

In Figure 2 we show penetration depth results in the progressive mode from 0.03 to 30.0 N. The unoriented samples show the shallowest depths, followed by parallel and perpendicular.

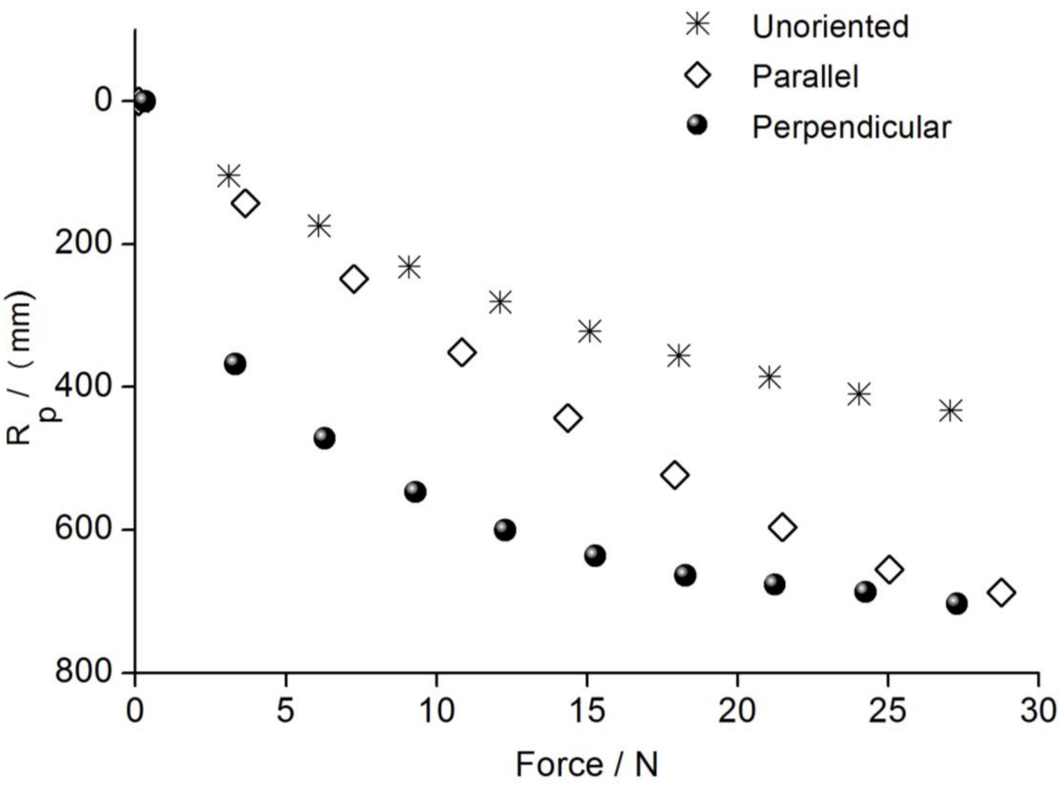

Fig. 2. Progressive scratching: penetration depth as a function of force.

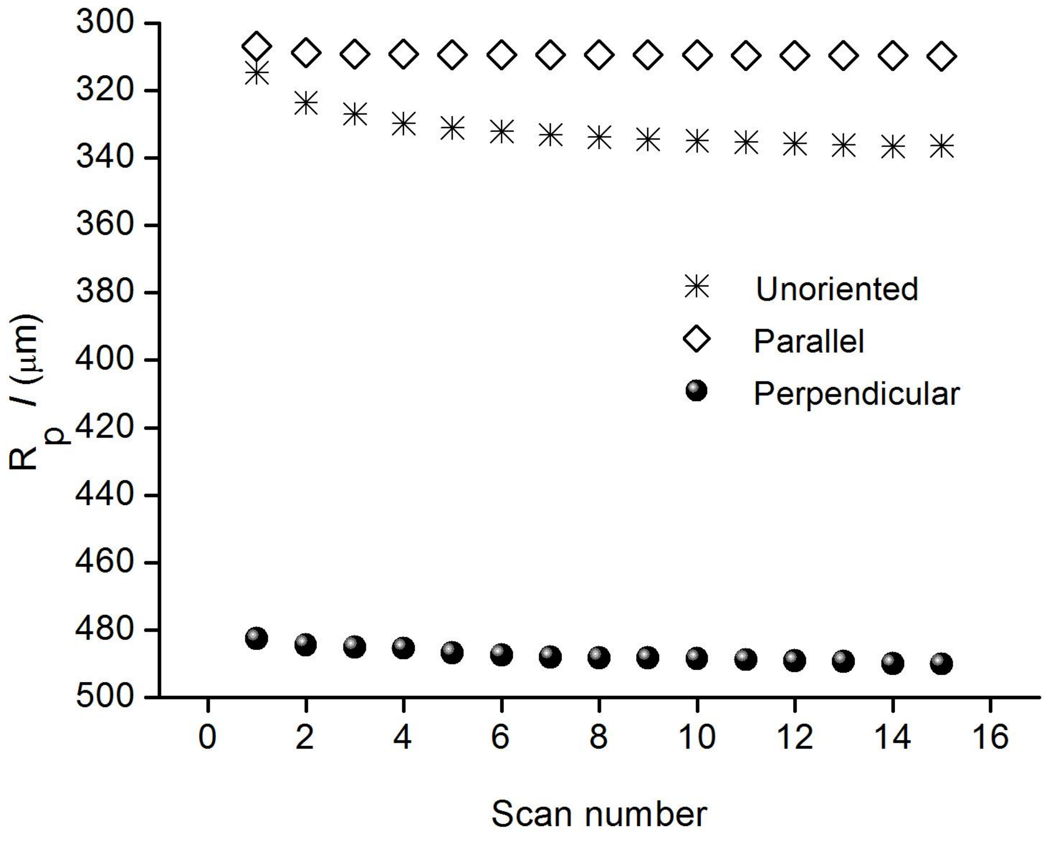

Fig. 3. Penetration depth in sliding wear as a function of the number of runs.

Scratch resistance

In Figure 3 we display the average penetration depths for sliding wear (multiple scratch experiments along the same groove) at 15.0 N as a function of the number of runs. Here the situation is different than for the penetration depths in Figure 2. Now the shallowest depths are seen for the parallel orientation. We also see here the phenomenon of strain hardening in sliding wear discovered first in 2004 [8] and explained in [41]. Apparently the densification demonstrated in [41] is the strongest along the orientation direction.

Figure 4 shows healing depths as a function of the test number. Here also the shallowest depths correspond to the scratching direction parallel to the orientation direction. The explanation is analogous; high concentration of polymer chains segments per unit volume around the groove counteracts strongly the action of the indenter. Thus, healing or recovery is a memory effect – here in tribology which is known well in mechanics. Clearly the chains which have 'survived' both uniaxial loading and scratching try to return as much as possible to their original locations.

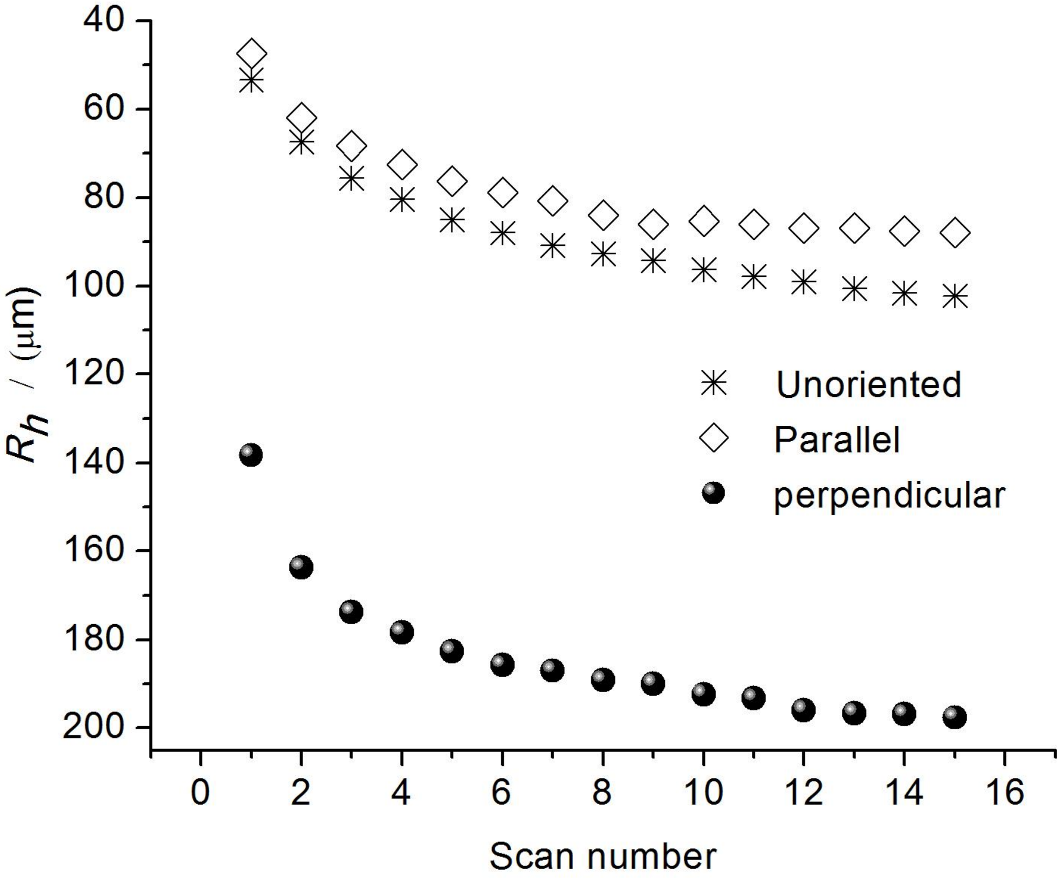

Fig. 4. Residual (healing) depth in sliding wear as a function of the number of runs.

In Figure 5 we show the percentage viscoelastic recovery *f* as defined by Eq. (1) plotted against the number of runs in sliding wear determination. The parallel orientation that has the shallowest depths in Figures 3 and 4 also exhibits the highest recovery – for the reason discussed above.

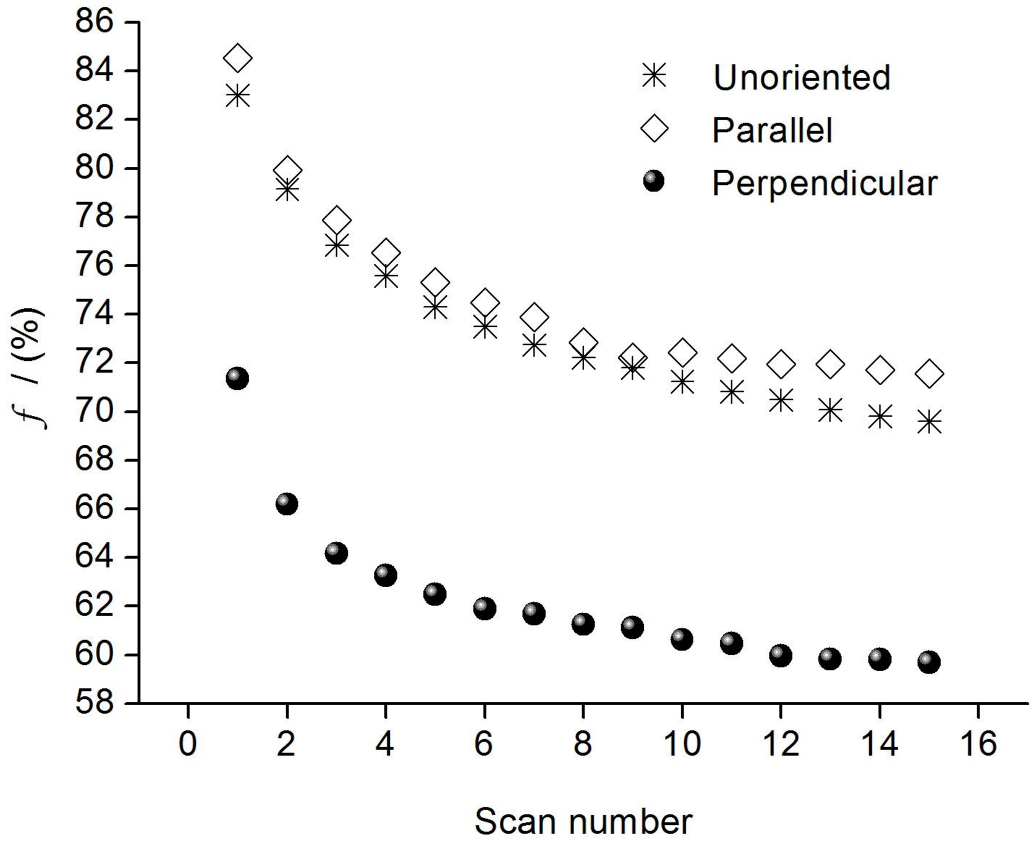

Fig. 5. Percentage recovery in sliding wear as a function of the number of runs for three types of samples defined in the insert.

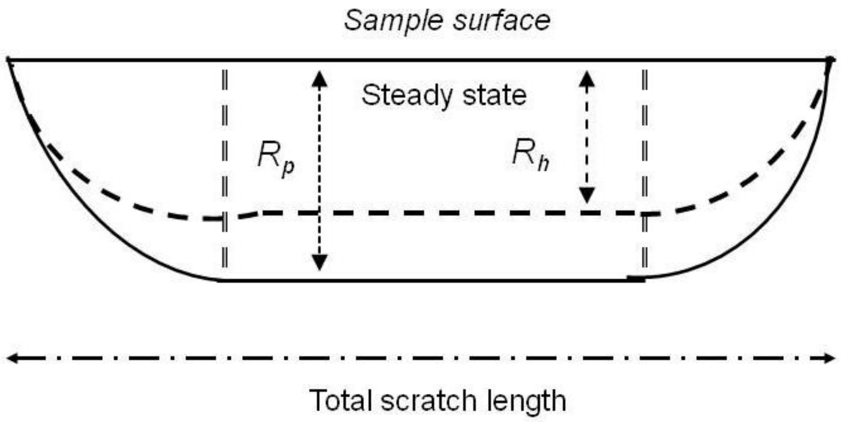

Fig. 6. A groove profile along the scratching direction; both the penetration depth and the residual depth shown.

General Discussion

The penetration depth by definition is the instantaneous depth immediately after the indenter 'hits' a given location. Consider the time when the indenter begins its trajectory that is on the left side in our Figure 6. The material directly to the right of the first point of contact of the indenter with the surface provides a *lateral reinforcement* to that point of contact. The situation is similar to that during nanoindentation [42] (or indentation in general); namely the locations around the point of contact are shallower than that point. Consider the indenter moving from left to right in scratch testing; gradually the ‘lateral support’ to the right of the original point of contact stops acting when the indenter keeps on moving away from that point. It is this situation that is schematically depicted in Figure 6. We recall here results of molecular dynamics computer simulation of scratch testing of non-crystals [4, 5]. Any location on the surface reaches quickly its penetration depth and then recovers gradually.

Since uniaxial loading as well as subsequent single scratch and/or sliding wear tests cause deformation of macromolecular chains, changes of conformations of those chains are involved. During the uniaxial orientation, the crystalline regions of LDPE align along the stretching tension - providing a storage modulus E’ in dynamic mechanical testing [42, 43] higher in that direction than in the perpendicular direction. The effects of the orientation on tribology have been seen in Figures 2 – 4; we shall now consider those results somewhat more in detail.

In sliding wear results presented in Figure 3 we see significant orientation effects. We recall once again results of a study of groove profiles perpendicular to the indenter trajectory [44]. There is formation of top ridges along that trajectory – and also densification at the bottom of the groove. The present results also support the conclusion that the densification is primarily responsible for the strain hardening.

Kopczynska and Ehrenstein [45] analyze effects of interfaces on properties of multiphase polymeric systems. In principle in our materials we also have two phases, crystalline and amorphous. However, in contrast to most multiphase systems, here the tie chains [46] result in ‘excursions’ of one phase into the other.

The differences of properties between oriented and unoriented samples can be explained in terms of the strength of intersegmental interactions. Along the orientation direction the indenter is ‘attacking’ a large number of covalent bonds C-C in the chain backbones. Perpendicular to that direction we have side chains; the interactions in that direction are largely of the van der Waals type, hence much weaker. Overall, scratching and sliding wear results are strongly affected by polymer orientation. This connection can be used at least in two ways: to use the scratching tests as a measure of orientation – and also to apply orientation to change tribological properties.

Polymer-based composites, including polymers reinforced with fibers, are applied more and more [47]. The presence of fibers induces a certain amount of orientation in processing. We also note that in multilayer composites low values of brittleness defined in Eq. (2) correspond to high structural integrity of the composite [48].

At the same time, the issue of wear increases in importance – in industry as well as in medical implants [49]. We conclude that microscratch technique is a powerful tool for evaluating tribological properties including wear, as well as viscoelastic recovery on polymer based materials. Moreover, this microscopic technique provides information about molecular orientation effects – including an increase in crystalline order (anisotropy) due to uniaxial extension of semicrystalline LDPE. Effects of the orientation changes caused by mechanical deformation are reflected in results of microscratch and sliding wear testing. We have thus demonstrated a new tool in the investigation of mechanical behavior of semicrystalline polymers. At the same time, imposition of molecular orientation in such polymers can be used to mitigate wear.

Experimental part

Materials

LDPE with the weight-average molecular weight $M_w \approx 2.0 \cdot 10^5$ and the mass density of 0.92 g/cm^3 was supplied in pellets by the Industria Cangrejera de México, Coatzacoalcos, Veracruz.

Sample preparation

Oriented LDPE samples were processed by injection molding as follows: 7 g of LDPE were introduced into an injector previously heated to 150 ^{o}C. After 10 min at this temperature the polymer was injected into a polished steel cubic mold heated to 100 ^{o}C. Samples were cut to 2.0 x 4.0 x 0.3 cm^3 sizes and tested in tension in a MTS TEST^{TM}/5 mechanical testing system at 40 ^{o}C for 8 hours until reaching 200 % fixed strain.

Unoriented samples were processed in square plates of 2.0 x 2.0 x 0.3 cm^3 by compressing molding at 120 ^{0}C for 15 min.

Micro-Raman analysis

A Jobin Yvon-Horiba Labram micro-Raman system (HR-800 LABRAM, France) consisting of a spectrometer with the grating of 600 groves/mm, an Olympus microscope (BX-41), a CCD Camera as detector and a polarized He-Ne (λ= 632.8 nm) laser as excitation source was used to perform the polarized Raman experiments. Lenses objective with a 50x magnification was used for focusing the laser beam on the sample and collect the back-scattered radiation. Spectra were recorded in air at room temperature.

Micro-scratch testing

(CSM Instruments^{TM}, Neuchatel, Switzerland) Micro Scratch Tester equipped with a diamond tip was used [2, 6 - 11]. First, a progressive load from 0.03 to 30.0 N was applied. Then 15 scans on the same groove were performed at the constant load of 15.0 N. In all experiments scratch length and scratch speed were kept constant, 7.0 mm and 10 mm/min, respectively. Recovery depths were measurements in the same scratch direction.

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References

[1] Rabinowicz, E. *Friction and wear of Materials*. Wiley, New York, **1995**.
[2] Brostow, W.; Deborde, J.-L.; Jaklewicz, M.; Olszynski, P. *J. Mater. Ed*. **2003**, 24, 19.

[3] Myshkin, N. K.; Petrokovets, I. M.; Kovalev, A. V. *Tribology Internat.* **2005**, 38, 910.
[4] Brostow, W.; Hinze J. A.; Simões, R. *J. Mater. Res.* **2004**, 19, 851.
[5] Brostow, W.; Simões, R. *J. Mater. Ed.* **2005**, 27,19.
[6] Brostow, W.; Bujard, B.; Cassidy, P. E.; Hagg, H. E.; Montemartini, P. E. *Mater. Res. Innovat.* **2002**, 6, 7.
[7] de la Isla, A.; Brostow, W.; Bujard, B.; Estevez, M.; Rodríguez, J. R.; Vargas, S.; Castaño, V. M. *Mater. Res. Innovat.* **2003**, 7, 110.
[8] Brostow, W.; Darmarla, G.; Howe, J.; Pietkiewicz, D. *e-Polymers* **2004**, no. 025.
[9] Bermudez, M. D.; Brostow, W.; Carrion-Vilches, F. J.; Cervantes, J. J.; Darmarla, G.; Pérez, J. M. *e-Polymers* **2005**, no. 003.
[10] Bermudez, M. D.; Brostow, W.; Carrion-Vilches, F. J.; Cervantes, J. J.; Pietkiewicz, D. *e-Polymers* **2005**, no. 001.
[11] Brostow, W.; Hagg Lobland, H. E.; Narkis, M.; *J. Mater. Res*. **2006**, 21, 2422. Brostow, W.; Hagg Lobland, H. E. *Polym. Eng. Sci.* **2008**, 48, 1982. Brostow, W.; Hagg Lobland, H. E. *J. Mater. Sci.* **2010**, 45, 242.
[12] Menard, K. P. *Dynamic Mechanical Analysis – A Practical Introduction,* CRC Press, Boca Raton, FL, **2008**.
[13] Raab, M.; Nezbedova, E. *Ch. 3 in Performance of Plastics,* Brostow, W.; editor, Hanser, Munich – Cincinnati, **2000**.
[14] Brostow, W.; Jaklewicz, M. *J. Mater. Res.* **2004**, 19, 1038.
[15] Martínez Antón, J.C.; Bernabeu, E. *Appl. Phys. Letters* **2002**, 80, 1692.
[16] Majumdar, H. S.; Bolognesi, A.; Pal, A.J. *Thin Solid Films* **2004**, 446, 296.
[17] Cayer-Barrioz, J.; Mazuyer, D.; Kapsa, Ph.; Chateauminois, A.; Robert, G. *Polymer* **2004**, 45, 2729.
[18] Karger-Kocsis, J.; Varga, J. *J. Appl. Polym. Sci.* **1996**, 62, 291.
[19] Karger-Kocsis, J. *Polym. Eng. Sci.* **1996**, 36, 203.
[20] Abraham, T.; Banik, K.; Karger-Kocsis, J. *Express Polym. Letters* **2007**, 1, 519.
[21] Rätzsch, M.; *Kunststoffe* **1998**, 88, 8.
[22] Alcock, B.; Cabrera, N. O.; Barkoula, N. M.; Loos, J.; Peijs, T. *Compos.* **2006**, 37, 716.
[23] Ospina, S. A.; Restrepo, J.; López, B. L. *Mater. Res. Innovat.* **2003**, 7, 27.
[24] Boiko, Yu.; Brostow, W.; Goldman, A. Y.; Ramamurthy, A.C. *Polymer* **1995**, 36, 1383.
[25] Lagaron, J. M.; Dixon, N. M.; Reed, W.; Pastor, J.M.; Kip, B.J. *Polymer* **1999**, 40, 2569.
[26] Sousa, A. R.; Amorim, K. L. E.; Medeiros, E. S.; Mélo, T. J. A.; Rabello, M. S. *Polym. Degrad. Stab*. **2006**, 91, 1504.
[27] Hashimoto, S.; Seki, K.; Sato, N.; Inkuichi, H. *J. Chem. Phys.* **1982**, 76, 163.
[28] Sambasivan, D.; Fisher, A.; Shen, M. C.; Hsu, S. M. *J. Biomed. Mater. Res. B* **2004**, 70, 278.
[29] Wang, A.; Sun, D.C.; Yau, S. S.; Edwards, B.; Sokol, M.; Essner, A.; Polineni, V. K.; Stark, C.; Dumbleton, J. H. *Wear* **1997,** 203-204, 230.
[30] Peterlin, A. *J. Mater. Sci.* **1971**, 6, 490.
[31] Michler, G.H. "*Deformation and fracture (Micromechanical Mechanisms)”* in: *Polymeric Materials Encyclopedia*, Salamone, J.S.; editor, CRC Press, New York, **1996**.
[32] Michler, G.H. *Kunststoff-Mikromechanik: Morfologie, Deformations- und Bruchmechanismen*, Carl Hanser, München, **1992**.
[33] Michler, G. H.; Adhikari, R.; Henning, S. *J. Mater. Sci.* **2004**, 39, 3281.

[34] Ward, I. M. *Structure and Properties of Oriented Polymers*, Chapman & Hall, London, **1998**.
[35] Pezolet, M. Pellerin, C.; Prud'homme, R.E.; Buffeteau, T.; *Vibr. Spectros.* **1998**, **18**, 103.
[36] Rodríguez-Cabello, J. C.; Merino, J.C.; Jawhari, T.; Pastor, J. M. *Polymer* **1995**, 36, 4233.
[37] Campbell, D.; Pethrick, R. A.; White, J. R. "Polymer Characterization, Physical Techniques", Stanley Thornes, London, **2000**.
[38] Bentley, P. A.; Hendra, J.P. *Spectrochim. Acta A* **1995**, 51, 2125.
[39] Lu, S.; Russel, A. E.; Hendra, J. P. *J. Mater. Sci*. **1998**, 33, 4721.
[40] Gall, J. M.; Hendra, P. J. *Spectrochim. Acta A* **1972**, 28, 1485.
[41] Brostow, W.; Chonkaew, W.; Rapoport, L.; Soifer, Y.; Verdyan, A. *J. Mater. Res*. **2007**, 22, 2483. Brostow, W.; Chonkaew, W.; Mirshams, R.; Srivastava, A. *Polymer Eng. Sci*. **2008**, 48, 2060.
[42] Beake, B. D.; Bell, G.A.; Brostow, W.; Chonkaew, W. *Polymer Internat*. **2007**, 56, 773.
[43] Brostow, W.; Chonkaew, W.; Menard, K.P. *Mater. Res. Innovat.* **2006**, 10, 389.
[44] Hongyi, Z.; Wilkes, G. L. *Macromolecules*, **1997**, 30, 2412.
[45] Kopczynska, A.; Ehrenstein, G.W. *J. Mater. Ed.* **2007**, 29, 325.
[46] Lustiger, A. *Ch. 16 in Performance of Plastics*, Brostow, W.; editor, Hanser, Munich – Cincinnati, **2000**.
[47] Bunsell, R.A.; Renard, J. *Fundamentals of Fiber Reinforced Composite Materials*, CRC Press, Boca Raton, FL, **2005**.
[48] Shen, J.; Wang, M.; Guo, S.; Xu, S.; Zhang, Y.; Li, T.; Wen, M. *Eur. Polymer J*. **2009**, 45, 3269.
[49] Gutmanas, E. Y.; Gotman, I. *J. Mater. Sci. Med.* **2004**, 15, 327.