Comparative Study of the Tribological Properties of Polyamide 6 Filled with Molybdenum Disulfide and Liquid Crystalline Additives

M. D. BERMÚDEZ, F. J. CARRIÓN-VILCHES, I. MARTíNEZ-MATEO, G. MARTíNEZ-NICOLÁS

Grupo de Ciencia de Materiales e Ingeniería Metalúrgica, Departamento de Ingeniería de Materiales y Fabricación, Universidad Politécnica de Cartagena, Campus Muralla del Mar, 30202 Cartagena, Spain

ABSTRACT: The effect of adding a 1 wt % proportion of thermotropic liquid crystals 4,4′-dibutylazobenzene (LC1) and 4-octyl, 4′-cyanobiphenyl (LC2) on the tribological properties of polyamide 6 (PA 6) is compared with that of the addition of MoS_2 in different concentrations (1 and 5 wt %). Friction and wear are determined in a pin-on-disk tribometer by using injection-molded additivated nylon disks against steel or aluminum pins, below (25°C) and above (80°C) glass transition temperature. Polymeric blends are characterized by differential scanning calorimetry and by optical and scanning electron microscopy and microanalysis. Concentration of liquid crystalline additives is higher at the surface than in the bulk of PA 6 disks. Crystallinity degree of PA-6 is not significantly changed by the presence of additives. Addition of 1 wt % LC1 improves processibility of PA 6 by increasing its melt flow rate. Cyanoderivative liquid crystal (LC2) shows the best wear-reducing ability for PA 6/steel contacts at all temperatures. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2426–2432, 2001

Key words: nylon (PA 6); sliding friction and wear; MoS_2; liquid crystal–polymer blends

INTRODUCTION

The use of polymers and polymeric composites in seals and bearings and other applications where tribological properties are important is growing rapidly.[1]

The growth of the worldwide plastics industry owes much to developments in additive technology.[2] Even plastics with excellent natural lubricity should be used with one or more antiwear additives.

Recently, a new class of self-reinforcing polymeric materials based on blends of isotropic thermoplastics and thermotropic liquid crystal polymers was developed.[3,4]

Nylons are used as gear and bearing materials because of their balance in strength, hardness, and toughness and because of their good friction properties. For such applications, nylons are filled with lubricating additives such as polytetrafluoroethylene (PTFE), silicone fluids, carbon fibers, graphite, molybdenum disulfide, and metallic powders.[3]

Lubricants in small amounts (usually <1%) can be used as melt-processing aids or, in larger proportions, to improve the properties of the end-use part. Lubricated nylons involve larger amounts (10–20%) of modifiers to improve the wear and friction characteristics of nylon parts. In both instances, surface rather than bulk properties are involved.

MoS_2 is a solid lubricant[4] having a lamellar or platelike crystal structure usually used in nylon composites to reduce wear rates and increase pressure–velocity (PV) limits.

Long-chain disubstituted azo derivatives belong to well-known thermotropic liquid crystals families,[5] and, besides their optoelectronic applications, they were investigated for their lubricating properties both as pure[6] and as lubricating oil additives.[7]

Cyanoaryl liquid-crystalline derivatives were extensively developed by their electrooptic properties as thermotropic liquid crystals.[5] Several authors[7–10] have also studied their lubricating ability in metal–metal contacts.

We have recently shown[11] that even polymers with poor self-lubricating characteristics, such as polystyrene (PS) or styrene acrylonitrile (SAN), can be more wear resistant when additivated with thermotropic liquid crystals, in particular with 4,4′-dibutylazobenzene (LC1).

In this work, we use 4-octyl, 4′-cyanobiphenyl (LC2) as polymer additive for the first time to compare its properties with that of the azo derivative.

The aim of the present work was to determine the capacity of liquid crystals to improve wear resistance of a self-lubricating polymer such as PA 6 used widely in tribological-demanding applications. We have compared the performance of the new additives with that of a classical nylon-lubricating additive such as MoS_2.

EXPERIMENTAL

Materials

Pellets measuring 3 mm of polyamide 6 ($[C_6H_{13}NO_2]_n$) and MoS_2 (powder, 99%, <2 μm size) were purchased from Aldrich (Milwaukee, WI).

LC1 was prepared[12] and purified[13] as previously described. LC2 was supplied by Merck (Poole, UK).

Pin materials were AISI 52100 steel and anodized aluminum ($R_a \leq 0.1$ μm).

Preparation and Characterization of Additivated PA 6 Disks

The nylon pellets were milled to powder and blended with the additive by using an IKA A-10 refrigerated mill equipped with tungsten–carbide blades. PA 6 pellets (8 g) were milled for 8 min. The additive (80 mg) was then blended by milling for another 8-min period. The final homogeneous powder has a mean particle size of <10 μm. Melt powder was injection molded at 250°C with a mold temperature of 130°C to obtain PA 6 disks.

PA 6 disks were kept in an atmosphere of controlled humidity, and water absorption was kept < 10% for every tested specimen.

Physical and Mechanical Properties of PA 6 Disks

Degree of crystallinity for additivated PA 6 was determined by differential scanning calorimetry (DSC)[14] in a Perkin–Elmer DSC-6 and the results are shown in Table I.

Melt-flow rate was determined according to ASTM D1238 standard, as the mean values of three measures with < 1% standard deviations.

At 25°C, a mean Shore D value of 77 was obtained for all additivated nylon disks, whereas heating at 80°C lowers hardness values to 65 Shore D. Roughness (R_a) for nylon disks was ≤ 0.5 μm.

Tribological Experiments

Tribological experiments were carried out on a pin-on-disk ISC 200PC tribometer with the following experimental parameters: pin radius = 0.34 mm; sliding radius = 10.5 mm; sliding distance = 1000 m; normal load = 7N; sliding speed = 0.1 m/s. The friction coefficient for each test was continuously recorded during the test time. Friction coefficients shown in Table II are mean values after three tests under the same experimental conditions.

For each additive, two sets of experiments were carried out, at 25 and 80°C, below and above the glass transition temperature, respectively.

Optical micrographs of additivated PA 6 were obtained with an Olympus BH2 microscope. Worn surfaces were observed under a JEOL 6100 SEM microscope and wear tracks measured by image analysis with a Leica DMRM microscope connected to an Optimas image analyzer. Wear vol-

Table I   Crystallinity of Additivated PA 6 as Determined by DSC

Additive (wt %)	LC1, 1%	LC2, 1%	MoS_2, 1%	MoS_2, 5%
Crystallinity degree (%)	23.31	23.47	22.65	21.90

Table II Friction Coefficients of Additivated PA 6/Metal Contacts [Load = 7*N*. Sliding speed = 0.1 m/s. Distance = 1000 m]

PA-6 Additive	Aluminum Pin		Steel Pin	
	25°C	80°C	25°C	80°C
LC1 1%	0.28 (0.02)	0.22 (0.002)	0.25 (0.05)	0.18 (0.02)
LC2 1%	0.30 (0.07)	0.21 (0.01)	0.22 (0.02)	0.23 (0.01)
MoS$_2$ 1%	0.30 (0.07)	0.23 (0.01)	0.26 (0.02)	0.25 (0.02)
MoS$_2$ 5%	0.20 (0.06)	0.21 (0.01)	0.28 (0.01)	0.25 (0.01)

umes were calculated by measuring wear track width,[15] as previously described.[11] Track widths are mean values after at least 12 measurements. Wear coefficients shown in Figure 2 are mean values after three tests for each material under the same experimental condition.

RESULTS AND DISCUSSION

Thermal Properties

Crystallinity percentages[14] were determined by DSC from the fusion heat of each sample with respect to that of the 100% crystalline material. The overall crystallinity percentage of the polymers is very similar (see Table I).

Melt-flow rate for LC1-additivated PA 6 is higher (66 cm^3/min) than for pure PA 6 (63 cm^3/min). This higher melt flow eases the injection-molding process, so this type of additive could have interesting scope as processing aids.

Another consequence of the presence of liquid-crystalline fluids during the injection processing of PA 6 disks is the distribution of the additive within the matrix.

Optical microscopy examination of the near-surface areas of thin films of LC-additivated nylon-6 shows that the distribution of the additives in the polymer matrix is not uniform. In fact, the additive is present in a higher proportion close to the surface. Figure 1 illustrates this effect for LC1-additivated PA 6. This figure shows an optical micrograph of a 50-μm-thickness film with a liquid-crystalline-rich surface layer between 30 and 60 μm thick.

This is, as far as we are aware, the first time this kind of filler-rich skin layer was characterized for liquid crystal/polymer blends. This observation could give rise to new surface-modified polymers with enhanced wear resistance without affecting the bulk properties of the base polymer.

Friction Coefficients

Friction coefficients are shown in Table II and vary between 0.18 and 0.30.

Literature values[16] for friction coefficients of nylon under dry wear against steel range between 0.25 and 0.6. A value of 0.35 was described[17] for PA 6 disks against mild steel pins in a triple pin-on-disk machine.

The friction and wear behavior of MoS$_2$-filled nylon was studied by many authors,[18] but results vary widely with test conditions and proportion of the additive.

From our data (see Table II), the effect of MoS$_2$ appears to be independent of temperature and concentration.

It is apparent that, under the conditions studied here, the addition of a 1 wt % of any additive
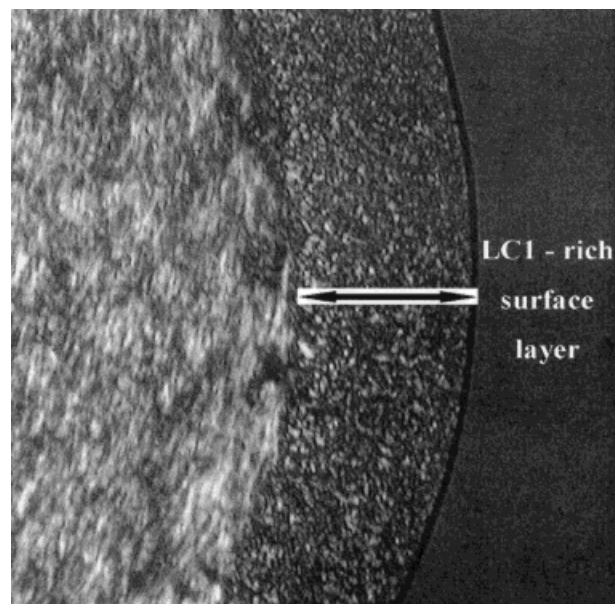

Figure 1 Crossed polarizers optical micrograph of 1% LC1 PA 6 film showing higher LC concentration close to the surface (PA 6 crystals appear white; LC1 appears gray).
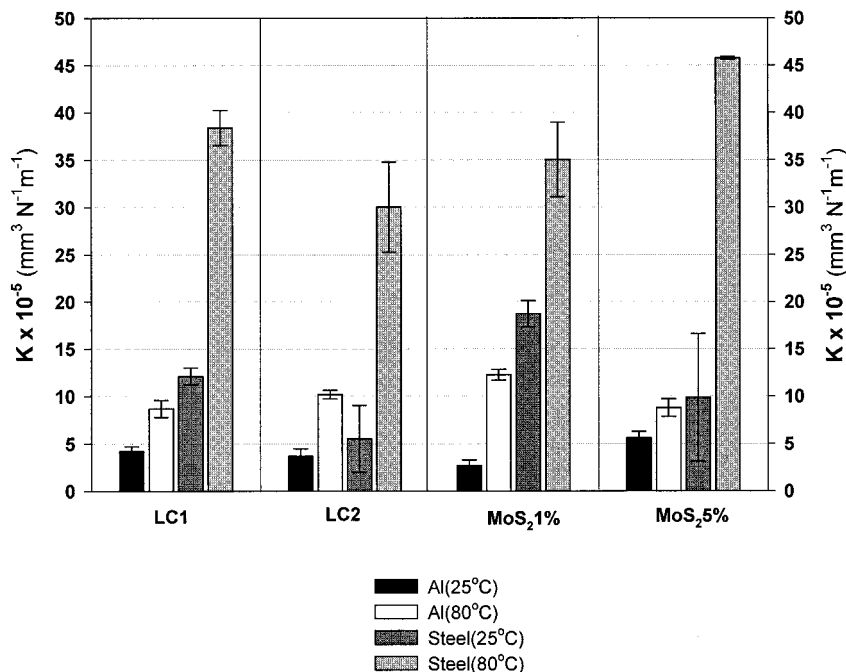
Figure 2   Wear coefficients for additivated PA 6 [Load = 7N; sliding speed = 0.1 m/s; distance = 1000 m].

has a similar effect on the friction coefficient of PA 6, regardless of the mating material and the temperature.

The only exception is that of LC 1 when sliding against steel at 80°C, which presents the lowest friction coefficient of all tests. At this high temperature (above the glass transition temperature), large deformations are produced in the PA 6/steel contact and segregation of the liquid-crystalline additive could give rise to an oriented lubricant layer in the contact zone.

The high polarity of the cyanoaryl molecules[19] of LC2, as compared with the apolar molecules of LC1, could account for their stronger interaction with the nylon matrix, making this additive less prone to segregation even at high temperature and, consequently, friction values for this additive are independent of temperature.

Wear Coefficients

Figure 2 shows wear rates (K, mm^3 N^{-1} m^{-1}) for each material and test conditions. For the materials studied here, severe wear ($> 20 \times 10^{-5}$ mm^3 N^{-1} m^{-1}) was only observed for PA 6/steel at 80°C. Steel pins remain unworn throughout the tests. In contrast, aluminum pin surfaces experience some volume loss (a mean value of 2.5 $\times 10^{-3}$ mm^3 after each test at 25°C).

LC2 shows good antiwear ability when compared (Fig. 2) with the other additives, particularly for PA 6/steel pairs.

We have previously described the good lubricating behavior of LC2 in aluminum/steel contacts when used as 1 wt % lubricating oil additive. This could be due to its ability to form adsorbed monolayers[20] onto the metal surface, particularly on steel pin surfaces that remain unworn throughout the tests.

Adsorbed monolayers of liquid crystals were observed by scanning tunneling microscopy (STM) techniques.[19]

Second harmonic generation methods have shown[20] that the liquid-crystal molecules exhibit a temperature-independent polar order on treated substrates with the principal axis inclined by a quasi-universal tilt angle of 60–80°, regardless of the method of surface treatment and the type of liquid crystal, concluding that polar ordering is confined to the first monolayer where almost all the molecules point their polar heads (the cyano groups of LC2) toward the solid substrate. This polar ordering rapidly decays into the bulk.[5,21]

Molecular alignment was recently demonstrated in liquid-crystalline-confined films,[22] revealing a profound dependence of the alignment on the applied stress.
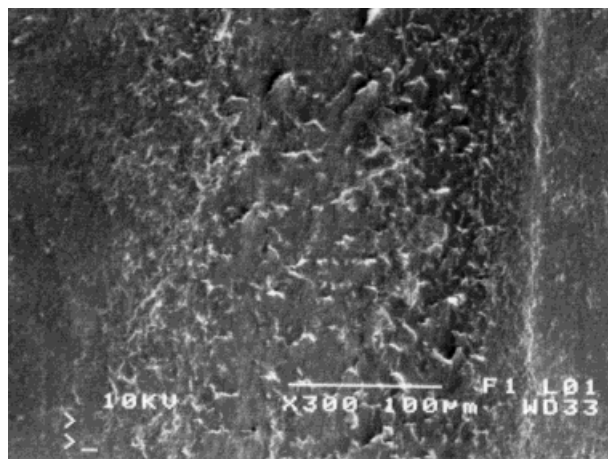
Figure 3 Wear track on 1% LC2 PA 6 disk (steel pin; 25°C).

Figure 4 Wear track on 1% LC1 PA 6 disk (aluminum pin; 25°C).

One percent LC2 shows even better antiwear performance than 5 wt % MoS$_2$ for PA 6/steel pairs (see Fig. 2). LC2 shows a slightly higher value of wear coefficient for PA 6/aluminum at 80°C, probably because the formation of oriented monolayers of LC2 molecules is disrupted by the wear of the aluminum pin.

Wear Mechanism

As can be seen in Figure 2, wear of PA 6/aluminum pairs are lower than that of PA 6/steel contacts even at 80°C. Thus, mechanical effects are predominant over thermal ones on the wear of PA 6. Only LC2 lowers the wear of PA/steel (Fig. 3) with respect to aluminum at 25°C, due to its high affinity for steel surfaces.

Under the conditions studied here, wear tracks are wider and smoother for PA 6/steel (Fig. 3) than for PA 6/aluminum contacts (Fig. 4), where large cracks can be seen inside the wear track.

Wear scars of PA 6 after sliding against steel (Fig. 3) and aluminum (Fig. 4) show significant differences. Figure 4 shows surface cracks transverse to the direction of sliding. This is in agreement with a fatigue–wear mechanism[23] and could be attributed to the fact that aluminum pins wear off during the tests, thus increasing surface asperities, whereas steel pins remain unworn.

For all four additivated PA 6 studied, the adhesive component of the wear mechanism is confirmed by observation of wear-debris particles (see Fig. 5) and transfer film adhered to metallic pin surfaces (Fig. 6).

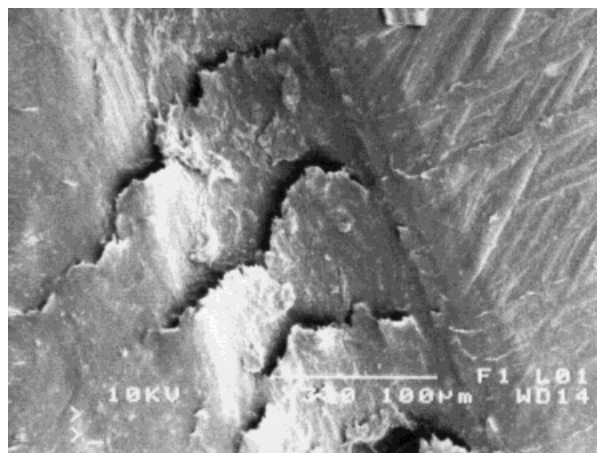The ribbonlike morphology of wear debris (Fig. 5) suggests that a significant thermal softening of the polymer,[24] combined with the transfer to the metallic pin, took place.

The high wear rate of MoS$_2$ additivated PA 6/steel contacts is illustrated in Figure 7, which shows sulfur concentration outside [Fig. 7(a)] and inside [Fig. 7(b)] the wear track.

CONCLUSION

1. Liquid-crystalline additives could be considered processing aid additives for PA 6. In fact, LC1 increases the melt-flow rate of PA 6, thus easing the injection process.

2. Injection-molded PA 6/liquid-crystal blends show filler-rich skin layers, giving rise to surface-modified polymers. This preferential distribution

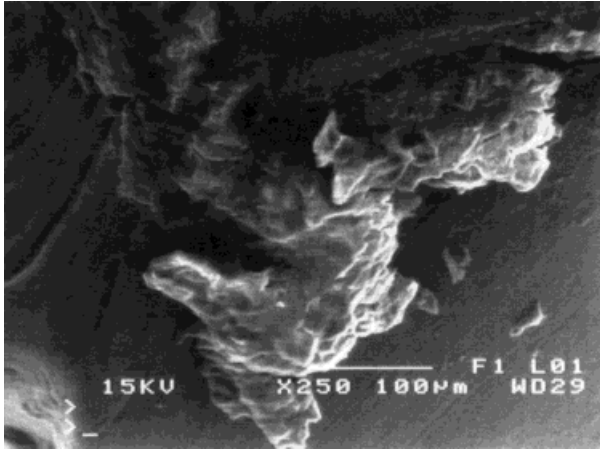**Figure 5** Ribbonlike wear debris on 1% LC2 PA 6 (steel pin; 80°C).

of liquid crystal at the surface does not affect base-polymer bulk properties such as crystallinity percentage.

3. For PA-6/steel contacts at 80°C (above glass transition temperature), the lowest friction coefficient is achieved when 1 wt % LC1 is added to PA 6, thus showing superior lubricating ability than 5 wt % MoS_2. This lubricating ability of LC1 could be due to its accumulation near the surface. This behavior could be favored by heating and applied stress during tribological tests.

5. For every additive, PA 6/steel contacts at 25°C and PA 6/aluminum contacts, at any temperature, experience mild wear with wear coefficients $< 2 \times 10^{-4}$ mm^3 N^{-1} m^{-1}.

A transition from mild to severe wear is observed for PA 6/steel contacts when heating from

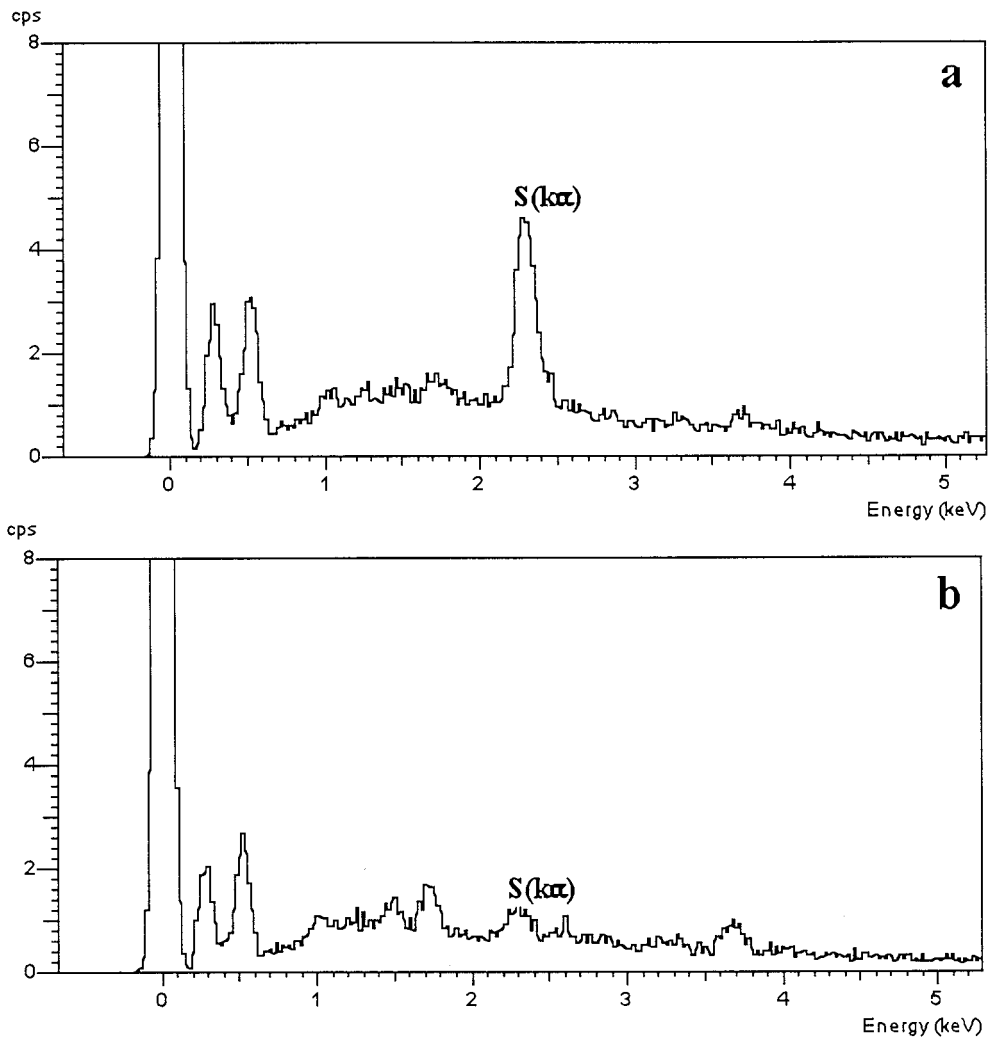**Figure 6** Wear debris adhered to aluminum pin (25°C).

Figure 7 Comparison of sulfur contents (a) outside and (b) inside the wear track for 1 wt % MoS_2-additivated PA 6.

25 to 80°C. The highest wear rate is observed for 5 wt % MoS$_2$.

The best antiwear additive for PA 6/steel contacts at 80°C is LC2, which reduces wear to a mean value of 3×10^{-4} mm^3 N^{-1} m^{-1}. This polar cyanoaryl liquid crystal also gives the lowest wear coefficient for PA 6/steel at room temperature, thus showing a special affinity for steel surfaces.

6. Although adhesion is the predominant wear mechanism for PA 6/steel contacts, wear of PA 6/aluminum contacts show a fatigue component. This could be related to the fact that aluminum pins experience some wear during the tests, whereas steel pins remain unworn.

REFERENCES

1. Williams, E. H.; Quinn, K. R. Mach Des 1995, 6, 50–52, 54.
2. Pritchard, G. Plastics Additives; Chapman and Hall: London, 1998.
3. Kohan, M. I. Nylon Plastics Handbook; Hanser: Munich, 1995.
4. Williams, J. A. Engineering Tribology (2nd ed.); Oxford University Press: New York, 1996.
5. Collings, P. J.; Patel, J. S., Eds.; Handbook of Liquid Crystal Research; Oxford University Press: New York, 1997.
6. Biresaw, G., Ed.; Tribology and the Liquid Crystalline State; American Chemical Society: Washington, DC, 1990.
7. Bermúdez, M. D.; Martínez-Nicolás, G.; Carrión-Vilches, F. J. Wear 1997, 212, 188–194.
8. Fisher, T. E.; Bhattacharya, S.; Salher, R.; Lauer, J. L.; Ahn, Y-J. Tribol Trans 1988, 31, 442–448.
9. Mori, S.; Ibata, H. Tribol Int 1996, 29, 35–39.
10. Yao, J.; Wang, Q.; Xu, Z.; Yin, J.; Wen, S. Lubr Eng 2000, 56, 21–25.
11. Bermúdez, M. D.; Carrión-Vilches, F. J.; Martínez-Nicolás, G. J Appl Polym Sci 1999, 74, 831–837.
12. Vicente, J.; Bermúdez, M. D.; Carrión, F. J.; Martínez-Nicolás, G. J Organomet Chem 1994, 480, 103–109.
13. Barrado, I.; Meseguer, V.; Bermúdez, M. D.; Martínez-Nicolás, G. J Supercrit Fluids 1997, 11, 73–80.
14. Bershtein, V. A.; Egorov, V. M. Differential Scanning Calorimetry of. Polymers; Ellis Horwood: Chichester, 1994.
15. ASTM G 99. Annu Book ASTM Stand 1990. [Standard test method for wear testing with a pin-on-disk apparatus.]
16. Bayer, R. G. Mechanical Wear Prediction and Prevention; Marcel Dekker: New York, 1994.
17. Thorp, J. M. Tribol Int 1982, 15, 69. [Friction, Lubrication and Wear Technology; in ASM Handbook, Vol. 18; ASM International: Ohio, 1992.]
18. Liu, W.; Huang, C.; Gao, L.; Wan, J.; Dang, H. Wear 1991, 151, 111–118 [and references therein].
19. Walba, D. M.; Stevens, F.; Parks, D. C.; Clark, N. A.; Wand, M. D. Science 1995, 267, 1144–1147.
20. Shen, Y. R. Liq Cryst 1989, 5, 635.
21. Noble-Luginbhul, A. R.; Blanchard, R. M.; Nuzzo, R. G.; J Am Chem Soc 2000, 122, 3917–3926.
22. Eisert, F.; Gurka, M.; Legant, A.; Buck, M.; Grunze, M. Science 2000, 287, 468–470.
23. Ovaert, T. C.; Ramachandra, S.; Trib Trans 1992, 40, 445–452.
24. Hosseini, S. M.; Stolarski, T. A. J Appl Polym Sci 1992, 45, 2021–2030.