

Friction and multiple scratch behavior of polymer + monomer liquid crystal systems

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Abstract

We have studied in turn: polystyrene (PS), styrene/acrylonitrile (SAN) and Polyamide 6 (PA6), adding each time to the polymer 1, 3, 5, 7 or 10 wt% of 4,4'-dibutylazobenzene (LC1) which is a monomer liquid crystal (MLC). LC1 reduces both static and dynamic friction of PS and SAN against stainless steels or polytetrafluoroethylene (PTFE). By contrast, friction values are lower for pure PA6 than for PA6 modified with various MLCs or with MoS₂.

Multiple scratching tests were carried out with a micro scratch tester on every system between 2.5 and 15 N. The presence of LC1 in PS reduces penetration depth and residual depth and increases the viscoelastic recovery. So far PS was the only polymer, which does not show strain hardening in multiple scratching. The present results confirms this, but it also shows that only 1 wt% of LC reduces the brittleness of PS so that strain hardening appears. This effect is maintained at all higher concentrations of LC1 investigated as well. For SAN or PA6, additions of LC1 reduce penetration depth values with respect to pure polymers, but do not have a significant effect on viscoelastic recovery. Scanning electron microscopy (SEM) was used to study the deformation and wear mechanisms, and to relate the data obtained in multiple scratch sliding wear tests. For PS we see in SEM that increasing the LC1 concentration causes a more ductile behavior, with less crack nucleation. For SAN the debris accumulation in sliding wear is mitigated by the presence of the liquid crystalline lubricant. No debris formation is observed in PA6, with or without a lubricant.

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1. Introduction and scope

Tribology is still much better developed for metals than it is for polymers. An exhaustive book on tribology by

Rabinowicz [1] deals with metals almost exclusively. The ongoing process in several industries of replacement of metal parts and components by polymeric ones is slowed down since polymeric surfaces undergo scratching and wear much more easily than metal surfaces. As pointed out by Rabinowicz [1], wear is a very serious economical problem, and thus even more acute for relatively 'weak' polymer surfaces.

Some progress in polymer tribology has been made, as reviewed in Ref. [2]. Let us try to make a list of existing options. Lowering friction and/or increasing scratch resistance of polymeric surfaces can reduce wear. The options are:

1 Using fillers [3]—which is a two-edged sword: in certain

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cases a filler enhances the scratch resistance; the usual explanation is enhanced adhesion of the transfer film to the counterface. Or else, the filler can weaken the scratch resistance. Similarly, fillers can either lower or else increase friction.

- 2 Using internal lubricants: the problem here is the rate at which the lubricant is oozing out from the bulk onto the surface. Too fast a rate would exhaust the supply of the lubricant from the bulk in less than the desired service time of the component. Too slow a rate would provide too weak effect on surface friction.
- 3 Converting polymers into heterogenous composites, for instance by putting in fibers. However, in carbon-fiber reinforced polymers the presence of fibers has been reported to *lower* the wear resistance as compared to neat polymers [4].
- 4 Formation of nanohybrids, either polymer matrix + ceramic powder with the size of particles <100 nm, or else analogous systems with metal powders.
- 5 External lubricants: in this case there exist a theory developed by Binienda, Pindera and coworkers [5–8] based on experiments with a well lubricated rigid punch of a parabolic profile, assuming fully frictionless contact. The theory is fairly general, tested for a variety of surfaces. However, in the case of polymers an external lubricant might cause swelling, and thus make the situation worse than was the case for the surface without a lubricant. We note here degradation of tribological properties caused by water aging as studied by Hodzic and coworkers [9,10]. At the same time, a judicious choice of external lubricants appears possible—a motivation for the present paper.

The present work represents a continuation of work on external lubricants conducted in Cartagena [11–13,15,16], work on friction [17], scratching and wear [18,19] at the University of North Texas (UNT), and also joint work of both groups [20,21]. Thus, the Cartagena group has demonstrated that monomer liquid crystals (MLCs) in base oils lower wear rates in steel+steel and steel+aluminum contacts [11]. Similarly, tribological properties of polystyrene (PS) and styrene/acrylonitrile (SAN) copolymer [12,15] as well as polyamide 6 (PA6) [13] have been modified using MLCs as lubricants. Ye and coworkers [14] reported fairly low friction values obtained using a ball-on-disk technique for metal pairs in the presence of fluorinated alkyimidazole borates, which are MLCs. They concluded that ‘ionic liquids exhibit superior tribological behavior’. However, using a pin-on-disk technique, our Cartagena group demonstrated that a non-ionic MLC provides at the ambient temperature and up to 80 °C or so better results than an ionic MLC lubricant [16]. A mixture of both kinds of lubricants can lower the wear of aluminum+steel even more [16]. Pin-on-disk tests for PS and SAN show that 1 wt% of a MLC improves the wear resistance of these polymers [12,15]. Similar results for PA6 [13] reveal a

similar or even superior antiwear property compared to the well known solid lubricant MoS₂.

In an earlier paper we have demonstrated lowering friction of a commercial epoxy by a fluoropolymer additive [17]. The results are strongly dependent, however, on the curing temperature of the epoxy. The same epoxy+fluoropolymer system was studied using a single scratch technique and a maximum in scratch resistance (shallowest residual scratch) found at the same concentration [18] at which the minimum friction is seen [17]. Sliding wear determination led to a discovery of strain hardening in multiple scratching [19] for three polymers. Recently the UNT and Cartagena groups have determined jointly the sliding wear multiple scratch resistance of pure PS, SAN, PA6 and polysulfones [20,21]. Except for PS well known for its brittleness, other polymers have also shown strain hardening that is an asymptotic residual depth plotted as a function of the number of tests performed. Thus, after 8–15 scratches, further scratching does not change the residual depth of the groove.

The results for pure polymers reported in [20,21] are followed in the present work by determination of static and dynamic friction and of multiple scratch resistance of PS, SAN and PA6 modified by the addition of variable proportions (from 1 to 10 wt%) of a thermotropic MLC, namely 4,4'-dibutylazobenzene (LC1), the same as used before [11,16]. In the case of PA6, the effect of 1 wt% LC1 has been compared with that of another MLC, namely 4-octyl 4'-cyanobiphenyl (LC2) [16] and with MoS₂.

2. Experimental

2.1. Materials

PS and PA6 were from Aldrich Chemicals Co. SAN was from BASF, Ludwigshafen/Rhein, Germany, and is known as Luran[®]. LC1 was synthesized [22], and purified [23] as previously reported. LC2 was supplied by Merck, MoS₂ (99%, powder, <2 μm) by Aldrich.

After milling the polymers with the corresponding proportion of MLC, PS and SAN samples were obtained by pressing the powders at 22 MPa while heating them at 150 °C in a Buehler metallographic press as previously described [13]. PA6 and PA6+MLC systems were injection molded at 250 °C also as described in [13].

2.2. Friction testing

A SINTECH machine with a friction attachment was used [17]. A 4.5 kg load cell and a sled with a nominal weight of 700 g were used. The testing speed was 150 mm/min. Polished AISI 52100 stainless steel or polytetrafluoroethylene (PTFE, Teflon) surfaces were used. Resistance to the initial and then continuous movement were measured to determine static and dynamic friction, respectively. The

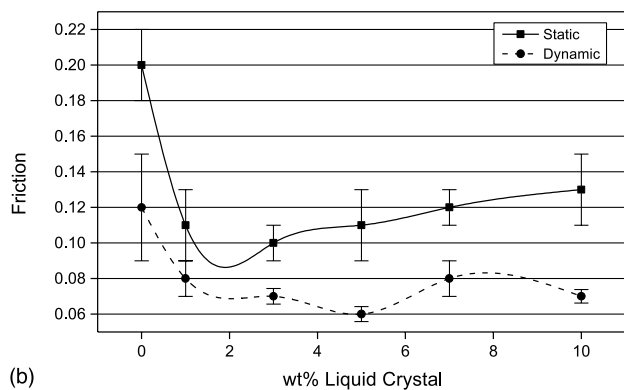
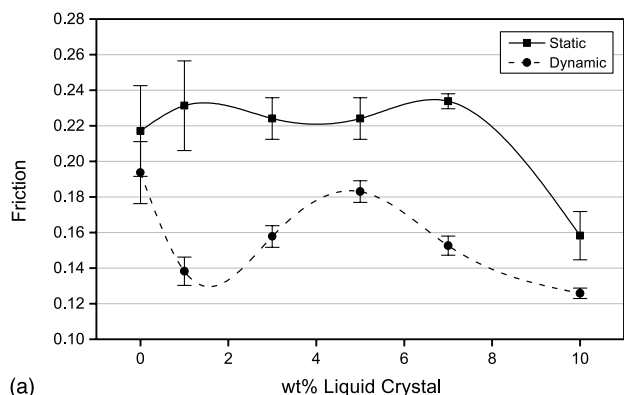


Fig. 1. Static and dynamic friction as a function of MLC content for PS + LC1 blends sliding against: (a) stainless steel; (b) PTFE.

results reported here are the averages of at least five tests at room temperature.

2.3. Scratch testing

The tests were carried out using a CSEM Micro-Scratch Tester (MST) and a procedure described in detail before [18, 19]. A minimum of 15 scratches were performed under the following parameters: normal load 2.5, 5, 7.5, 10, 12.5 and 15 N, scratch length 5 mm, scratch velocity 2.5 mm/min at the room temperature. A conical diamond indenter was used in all the tests with the diameter of 200 microns and the cone angle of 120° [20]. The results include the penetration (instantaneous) depth R_p and the residual (healing) depth R_h . Repetitive experiments have confirmed that the shallower residual depth in our viscoelastic materials is reached inside 3 min. Therefore, R_h values have been in each case determined 5 min after recording the R_p values. The results presented are averages from a minimum of 15 scratches along several locations on a given sample.

2.4. Scanning electron microscopy (SEM)

Jeol JSM T-300 and Hitachi 3500-N scanning electron microscopes (SEMs) were used. The samples were sputter

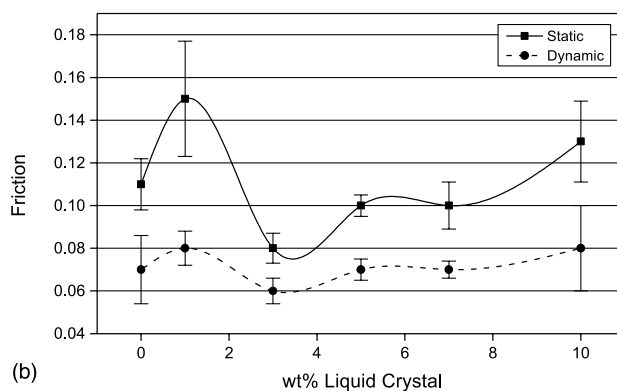
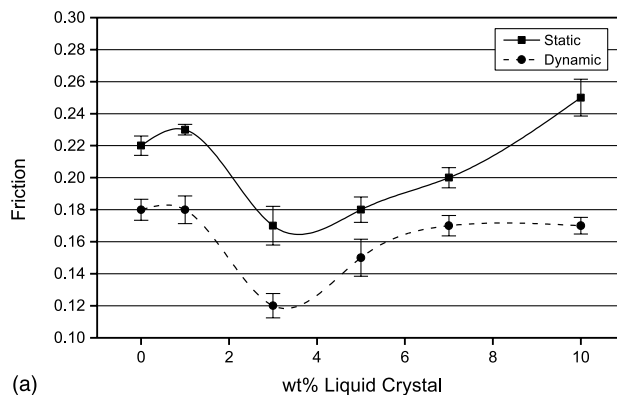


Fig. 2. Static and dynamic friction as a function of MLC content for SAN + LC1 blends sliding against: (a) stainless steel; (b) PTFE.

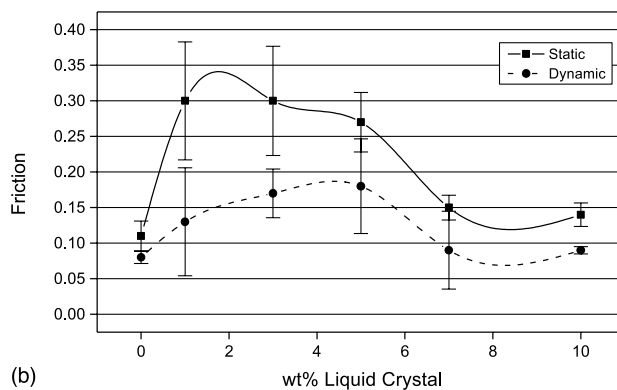
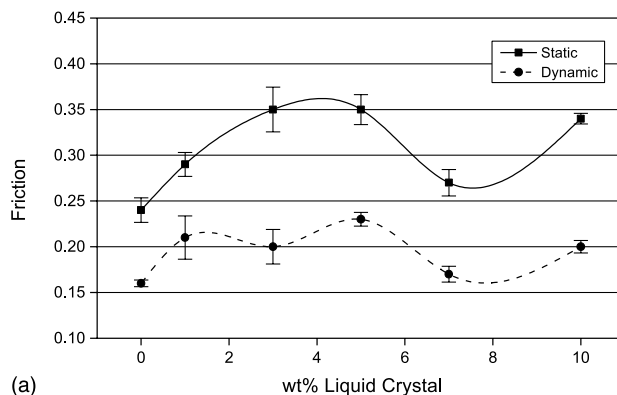


Fig. 3. Static and dynamic friction as a function of MLC content for PA6 + LC1 blends sliding against: (a) stainless steel; (b) PTFE.

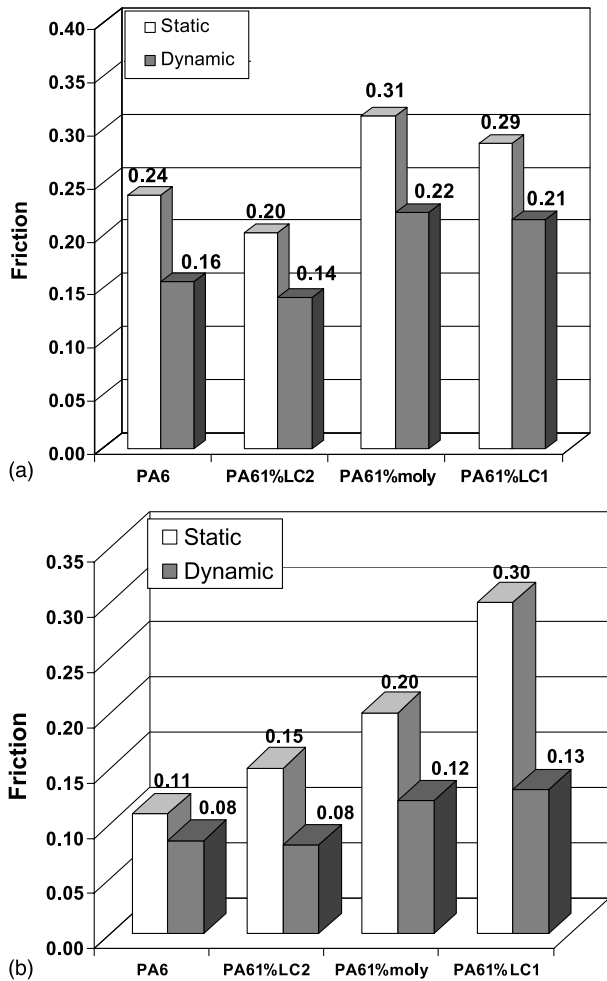


Fig. 4. Influence of 1 wt% LC1, LC2 and MoS₂ fillers on static and dynamic friction of PA6 against: (a) stainless steel; (b) against PTFE.

coated with a thin layer of gold in order to make them conductive with the aid of a SC7640 Sputter Coater of Polaron Division.

3. Friction results

We have previously reported [13,15] tribological properties of PS and SAN with LC1 additions in pin-on-disk tests against AISI 52100 steel under variable load, speed and sliding distance. We have found that addition of 1 wt% LC1 produces a dynamic friction reduction with respect to pure PS between 10 and 14%, depending upon test variables. A maximum friction reduction of 17% is obtained when 10 wt% LC1 is added [24].

Fig. 1(a) shows static and dynamic friction determined as described in Section 2.2 for PS and PS+LC1 blends against the stainless steel. Maximum reductions of 37.5% in static friction and 31.6% in dynamic friction are observed for the highest 10 wt% concentration of LC1.

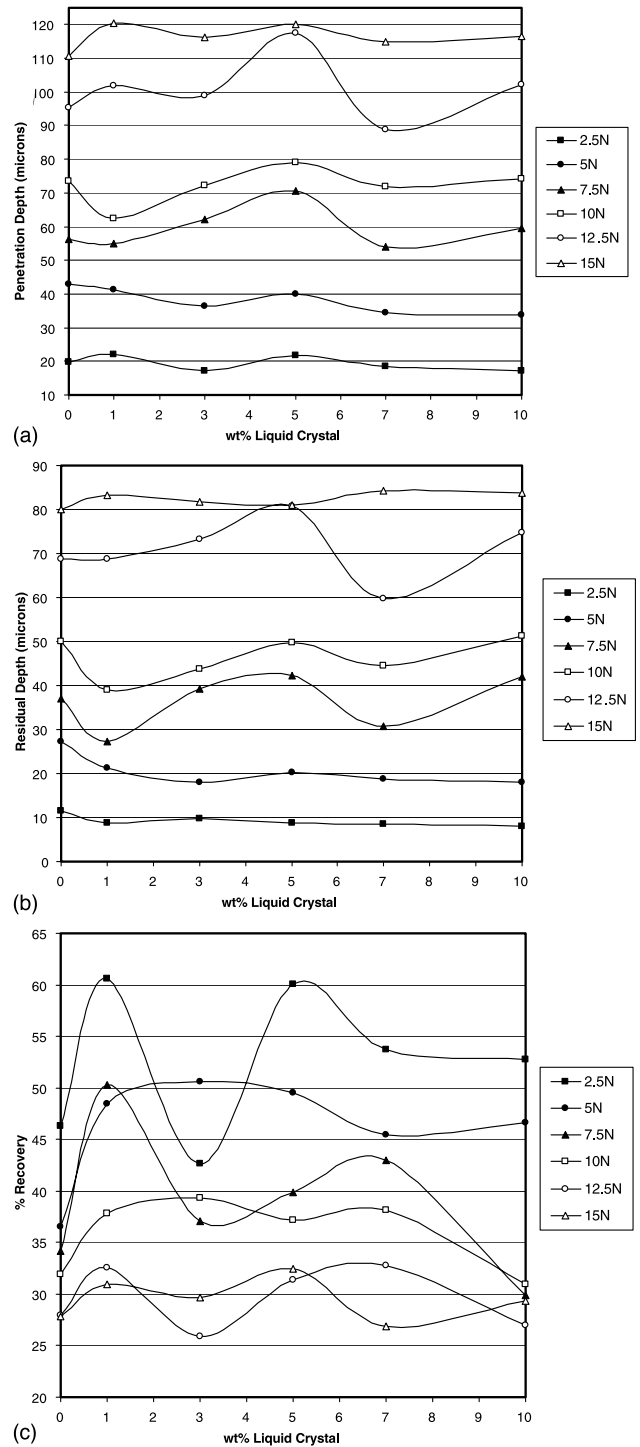


Fig. 5. Scratch resistance after 15 scratches of PS+LC1 blends under variable load. (a) Penetration depth; (b) Residual depth; (c) viscoelastic recovery.

In the case of PS+PTFE contacts (Fig. 1(b)), the addition of 1 wt% LC1 lowers the static friction against PTFE by 45% with respect to pure PS, and the dynamic friction by 35%. Maximum reduction in static friction

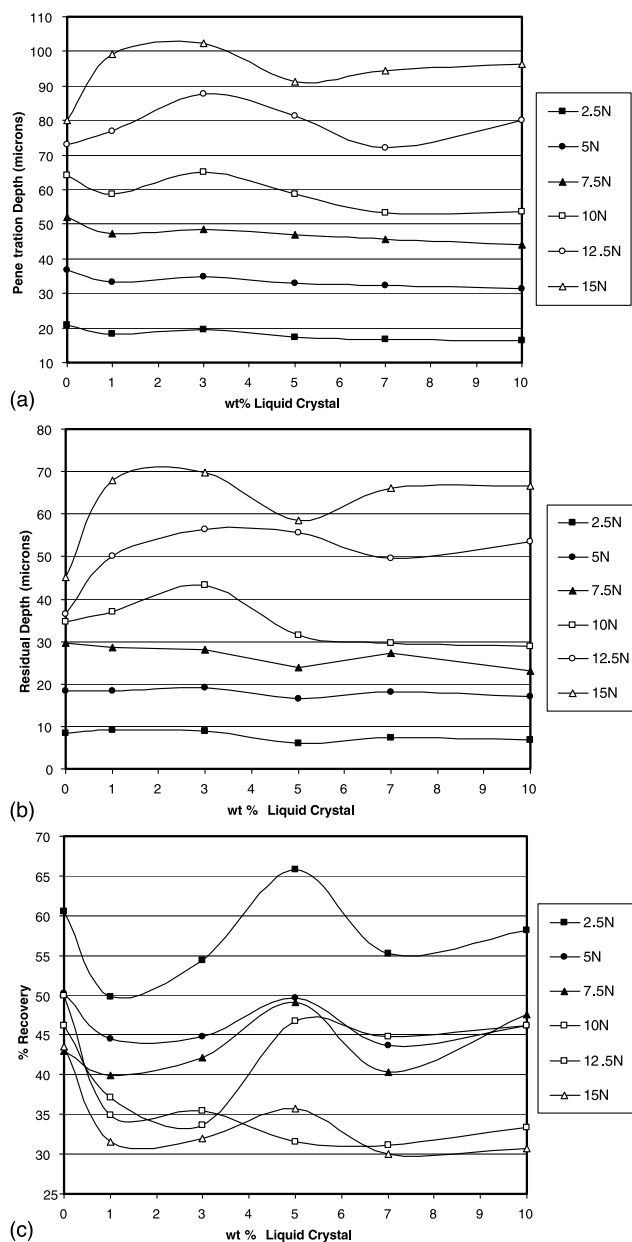


Fig. 6. Scratch resistance after 15 scratches of SAN+LC1 blends under variable load. (a) Penetration depth; (b) residual depth; (c) viscoelastic recovery.

(49%) is reached for 3 wt% LC1 and in dynamic friction (42%) for 5 wt% LC1. Further increments in LC1 content lead to friction increases; we recall extrema in the friction vs. the additive concentration curves for the epoxy + fluoropolymer system studied in [17].

In our friction experiments, the surface characteristics determine the friction values. We recall the connections of static and dynamic friction and also of penetration and residual depths to the surface tension for epoxy + fluoropolymer systems [25]; extrema in all these five properties appear at the same concentration. We also note that in our

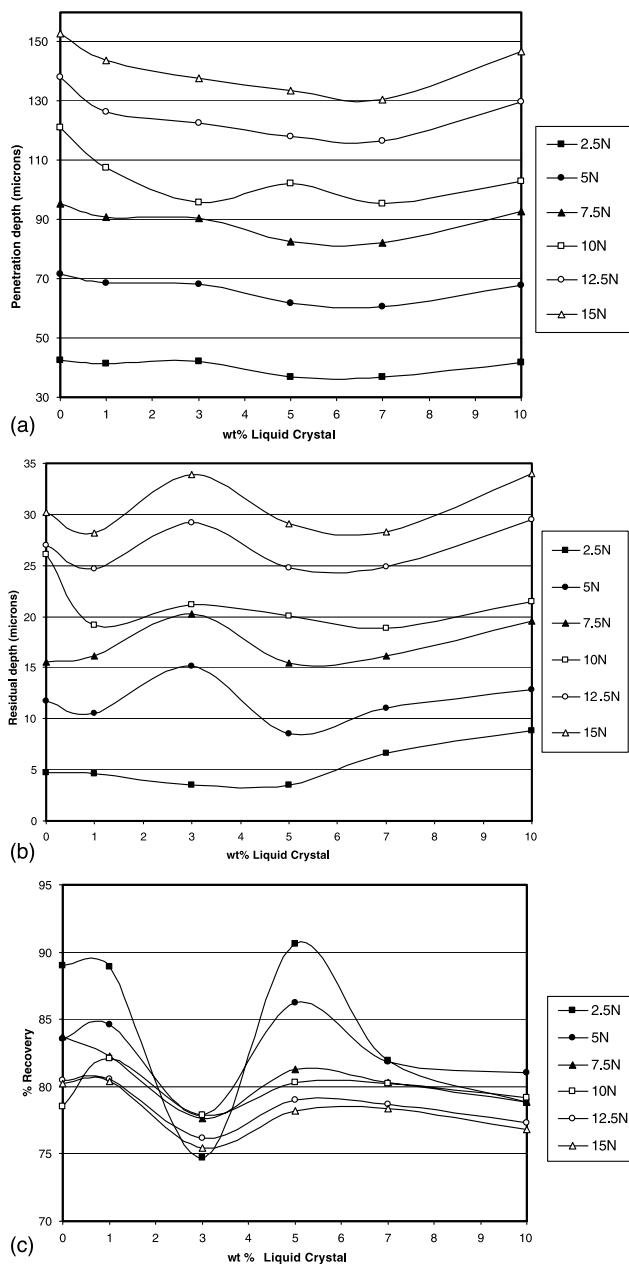


Fig. 7. Scratch resistance after 15 scratches of PA6+LC1 blends under variable load. (a) Penetration depth; (b) residual depth; (c) viscoelastic recovery.

friction tests no significant loss of material takes place—in contrast to wear in the pin-on-disc testing conditions.

Adding LC1 reduces static and dynamic friction of PS against PTFE (Fig. 1(b)) because of the presence of the MLC at the surface. Further addition of the liquid crystal modifies the bulk structure [15] but less so the surface.

In the case of SAN+LC1 blends sliding against stainless steel (Fig. 2(a)), minimum friction values are obtained for the 3 wt% LC1 content, with a 23% reduction in static friction and a 33% reduction in dynamic friction values with

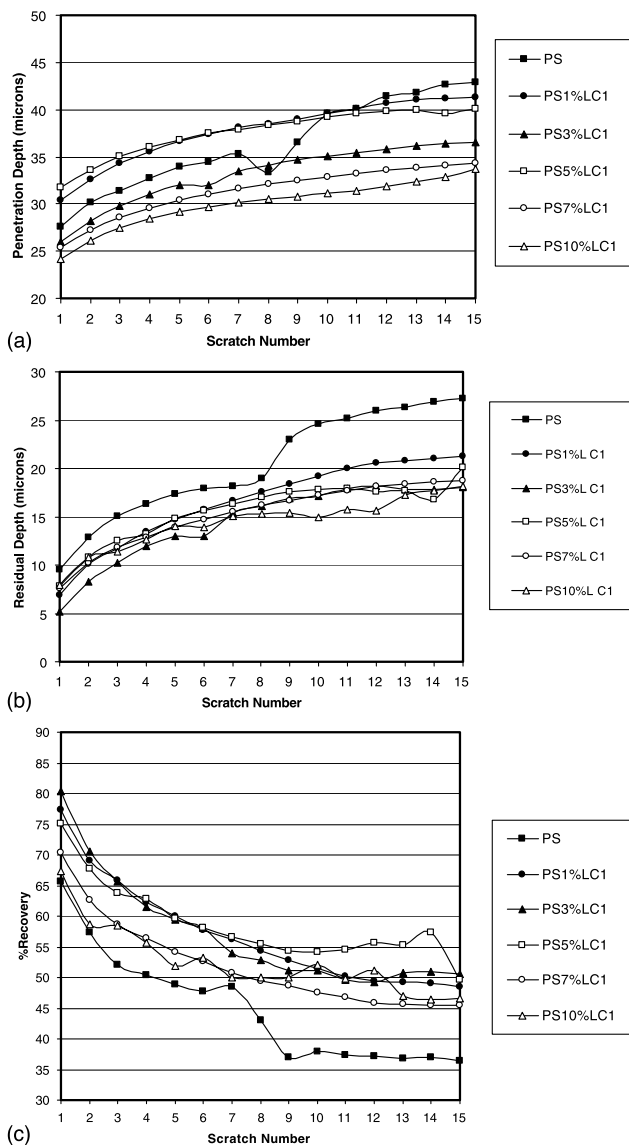


Fig. 8. Scratch resistance of PS + LC1 blends as a function of the number of scratches. (a) Penetration depth; (b) residual depth; (c) viscoelastic recovery.

respect to pure SAN. When sliding against PTFE (Fig. 2(b)), the addition of LC1 results in 31% reduction in static friction and 21% reduction in dynamic friction with respect to pure SAN.

A more than 30-years old paper by Briscoe and coworkers [26] explains the mechanism of liquid lubrication by organic molecules in terms of sliding of the chains lengthways over one another. We find this explanation not only convincing but also supported by the results of Ye and coworkers [14] and by our own results. The MLC liquids used by Ye provide some lubrication; the ionic character of the liquids gives a certain amount of adhesion to metal surfaces (Ye and his colleagues do not define their 'friction

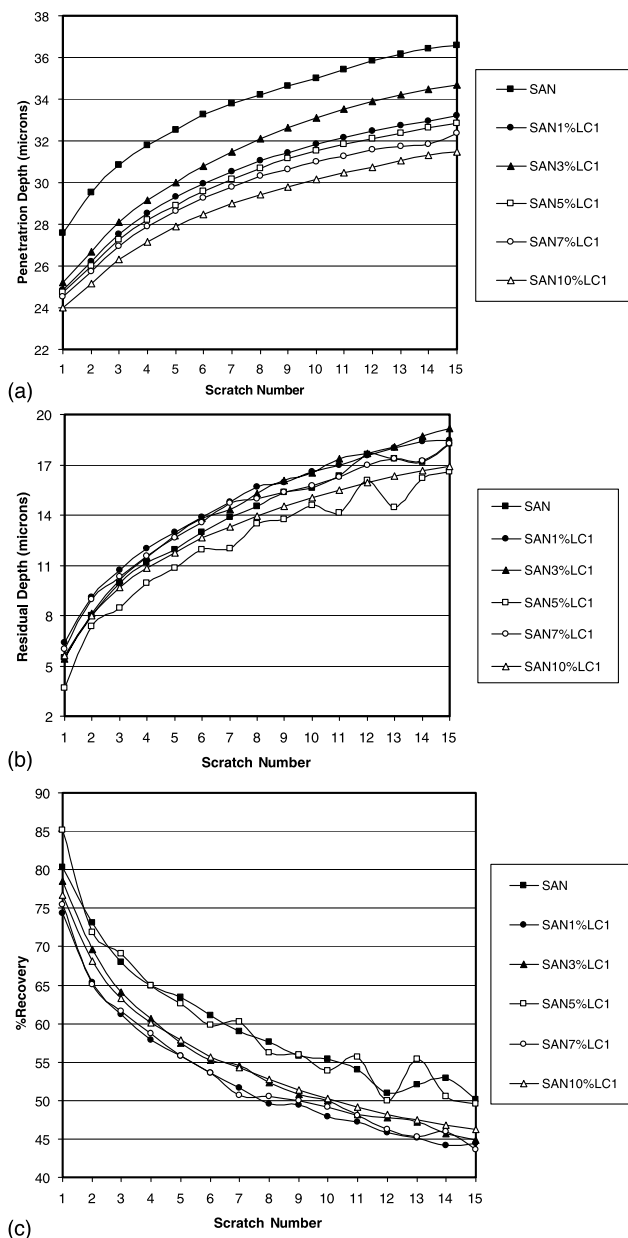


Fig. 9. Scratch resistance of SAN + LC1 blends as a function of the number of scratches. (a) Penetration depth; (b) residual depth; (c) viscoelastic recovery.

coefficients' as either static or dynamic). As reported in [16], the non-ionic liquid crystalline lubricant LC1—which we now also use—gives at room temperature lower friction values than an ionic MLC. Since liquid crystal chains undergo orientation naturally [27], the sliding mechanism of Briscoe [26] is enhanced. In other words, MLCs exhibit two advantages over other organic molecule lubricants: the oligomeric chain character and the ease of orientation.

A different behavior to that described for PS and SAN is observed for Polyamide-6. Already for SAN we have seen that addition of the LC1 lubricant causes first an increase of

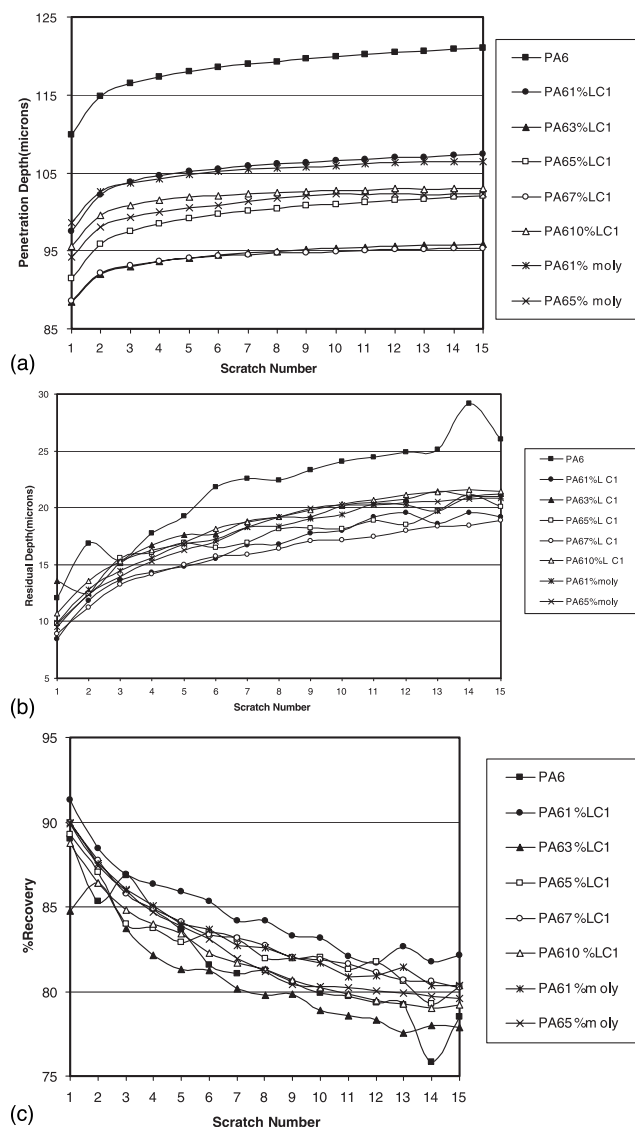


Fig. 10. Scratch resistance of PA6+LC1 blends as a function of the number of scratches. (a) Penetration depth; (b) residual depth; (c) viscoelastic recovery.

both static and dynamic friction, this against AISI 52100 steel as well as Teflon. However, subsequent addition of the lubricant produces friction values lower than for the polymer without the lubricant, again for steel as well as for Teflon. In the case of Polyamide-6 we see similarly a first increase and then a decrease in friction values. The maxima are broader than for SAN. More importantly, the subsequent minima represent higher values than for the un-lubricated polyamide. The objective of lubrication is not achieved. The respective results for PA6+stainless steel and PA6+PTFE contacts are shown in Fig. 3(a) and (b), respectively.

Given the results displayed in Fig. 3, we have also studied influence of other additives on the friction behavior of PA6. Fig. 4 shows the comparative results for pure PA6,

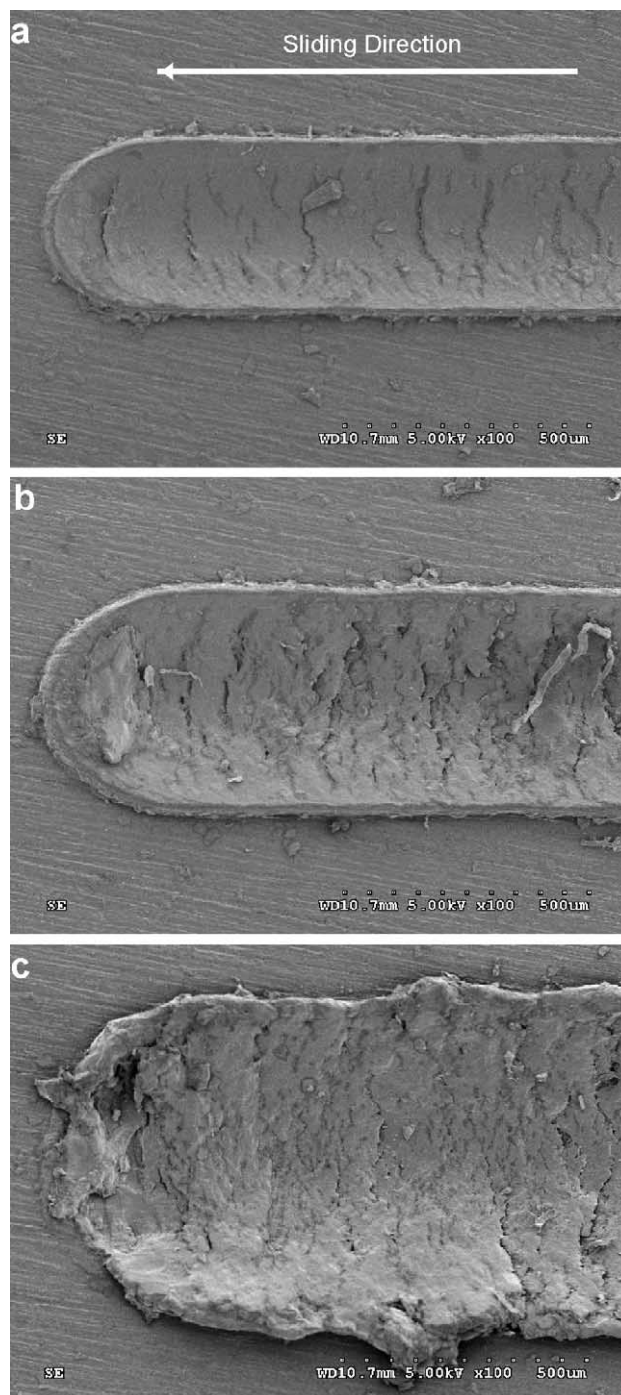


Fig. 11. SEM micrographs of the multiple scratch surface on PS+1% LC1 under increasing load: (a) 5 N; (b) 7.5 N; (c) 15 N.

PA6+1 wt% LC1, PA6+1 wt% LC2 and PA6+1 wt% MoS₂, these against stainless steel in Fig. 4(a) and against PTFE in Fig. 4(b). We find that a 1 wt% addition of MoS₂, a well known solid lubricant, increases friction of PA6. Among the materials investigated, only LC2—which is also a non-ionic MLC—causes a reduction in static and dynamic

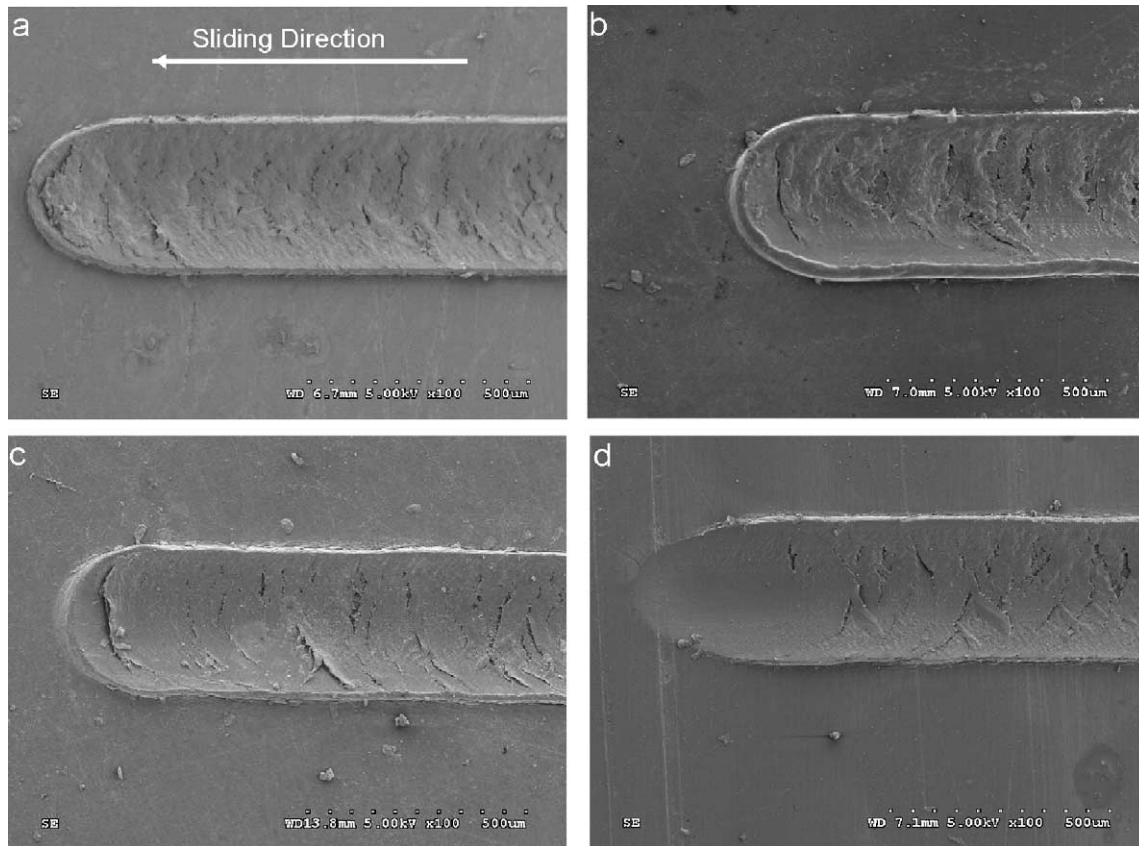


Fig. 12. SEM micrographs of the multiple scratch surface on PS under 5 N as a function of LC1 content: (a) Pure PS; (b) PS + 3% LC1; (c) PS + 7% LC1; PS + 10% LC1.

friction of PA6 when sliding against stainless steel, but not against PTFE.

These results can be explained by the fact that polyamides are known to have good autolubricating properties derived from their ability to form transfer films on the counterface of the mating material. Thus, a further improvement by lubricants is more difficult. In contrast, PS and SAN are polymers with poor autolubricating ability. We also recall that PS- and SAN-based blends have been prepared by compression molding while PA6-based materials were obtained by injection molding.

The results in Fig. 3 (broad maxima) and those in Fig. 4 can be also connected to those reported in Ref. [15]. It has been shown then that PA6 + 1 wt% LC1 blends prepared by injection molding show a concentration gradient of the MLC, namely the additive accumulates at the surface. High concentration of the low molecular weight additive at the surface might disrupt the transfer layer from PA6 to the counterface, thus reducing the good autolubricating ability of the base polymer.

4. Sliding wear results

Given the importance of wear noted in the beginning of the present paper, and also the discovery of strain hardening in multiple scratching for several polymers [19,20], we have performed multiple scratching tests along the same original groove. Thus, we have investigated wear by multiple sliding.

4.1. Effects of varying load and lubricant concentration

In Ref. [20] we have reported sliding wear results for the low applied force of 5.0 N and a single scratching velocity of 2.5 mm/min at the room temperature. In Ref. [21] we have extended this work to study effects of varying the velocity from 1.0 to 15.0 mm/min, also under 5.0 N and at the room temperature. Now we have extended our work further by covering a series of forces applied, from 2.5 to 15.0 N. As stated in Section 2.3, we have retained the scratch velocity 2.5 mm/min at the room temperature.

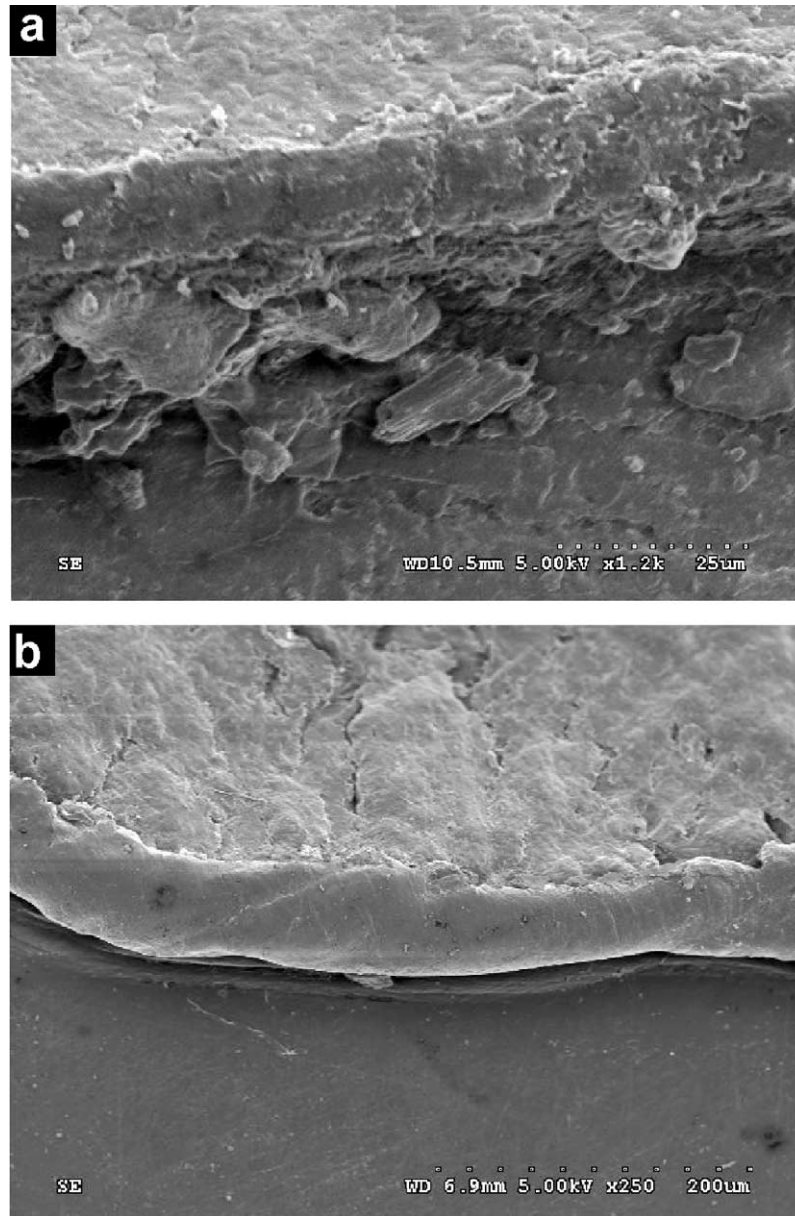


Fig. 13. (a) SEM images of PS+10% LC1 after 15 scratches under 2.5 N showing parallel cracks convex to the sliding direction. (b) Magnification ($\times 500$) showing cracks and wear debris. (c) Magnification ($\times 1200$) showing wear particle detachment from the crack edge.

Fig. 5 shows the results for PS for several loads in terms of the penetration depth R_p (Fig. 5(a)), the residual depth R_h (Fig. 5(b)) and the viscoelastic recovery ϕ (Fig. 5(c)) obtained after 15 scratches for PS and PS+LC1 blends as a function of the normal applied load and the LC1 content. The viscoelastic recovery has been defined [17] as

$$\phi = (1 - R_h/R_p) \times 100\% \quad (1)$$

As argued in [20], the residual depth is a practical measure of the scratch resistance. Therefore, we focus first on Fig. 5(b). We see either fairly flat curves of R_h as a function

of LC1 concentration, or else minima around 1 wt% LC1. This observation is reinforced by Fig. 5(c) in which we see maxima of the viscoelastic recovery ϕ at that concentration. As expected, lower the applied force, higher the recovery. The existence of maxima and minima in Fig. 5(c) deserves an explanation. We recall the results reported in [15] and already referred to at the end of Section 4: the MLC additive accumulates at the surface. Thus, when LC1 is added to the pure PS, first it apparently provides recovery enhancement. When more MLC than 1% is added, MLC aggregation at the surface and MLC island formation is possible. The islands

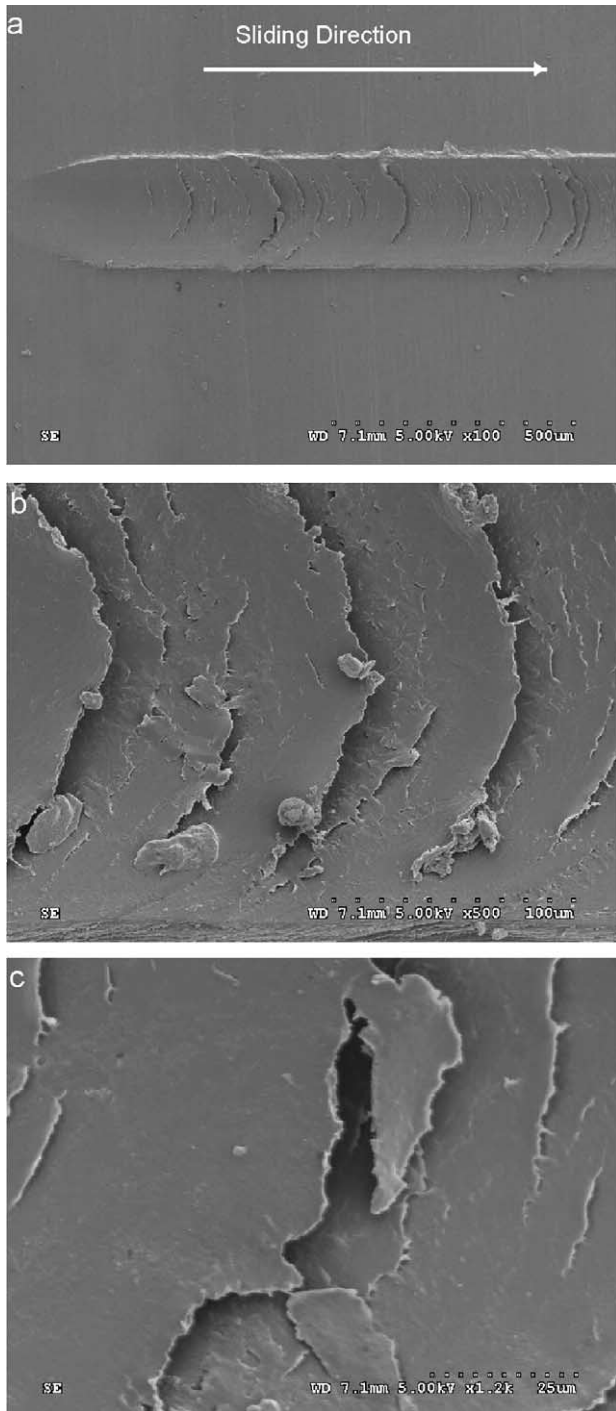


Fig. 14. (a) SEM image of the scratch surface on PS+3% LC1 after 15 scratches under 12.5 N and detail of wear debris. (b) Magnification ($\times 1200$) showing wear particle morphology.

would make lesser contribution to the viscoelasticity of otherwise brittle polystyrene. Only when we add still more LC1, above 3 wt%, the MLC would partly go into the islands and partly interact with PS helping recovery; the

overall recovery effect increases again. A desired result seen in Fig. 5 is the fact that already 1% of LC1 produced the residual depth lowering as well as higher ϕ .

In turn, in Fig. 6 we display the results for SAN. The LC1 lubricant is not exactly effective here. Either it makes no difference to the residual depth or even at higher loads makes the depth even larger (Fig. 6(b)). The lubricant initially lowers the viscoelastic recovery, but there is a recovery maximum at 5% LC1 (Fig. 6(c)).

We now consider the results for PA6 (Fig. 7). There are minima of the residual depth at 1% and $\approx 5\%$ LC1 (Fig. 7(b)). The minima correspond to maxima of the recovery ϕ in Fig. 7(c). The minima and maxima in Fig. 7(c) can be explained by a mechanism similar to that discussed in connection with Fig. 5(c).

It is instructive to compare results for the three polymers with the LC1 lubricant. We conclude that PS has the lowest scratch resistance in terms of R_h . This fits well with the fact that PS is quite brittle, in contrast to the other polymers.

4.2. Effects of the number of scratches

The results presented above pertain to 15 scratches. We now report results as a function of the number of scratches. We begin again with polystyrene; the results for several concentrations of LC1 under 5.0 N are shown in Fig. 8.

We have reported before [20] that PS is an exception among all polymers investigated so far, namely it does not show a horizontal asymptote in scratch depth values as a function of the number of tests. A transition to more severe wear occurs around eight or nine passes. In other words, there is no strain hardening in multiple sliding along the same groove. Fig. 8 shows that the addition of only 1% of LC1 produces a dramatic result: the strain hardening appears—and it persists at all higher LC1 concentrations investigated. The presence of LC1 in any proportion decreases both the penetration and the residual depths. After 15 scratches, PS+10% LC1 shows the 21.3% reduction in R_p (Fig. 8(a)) and the 33.4% reduction in R_h (Fig. 8(b)) with respect to PS.

The pure SAN copolymer is a well behaving one, and does show strain hardening in the sliding wear [20,21]. We now show results for several SAN+LC1 concentrations as a function of the number of scratches in Fig. 9. Any concentration of LC1 lowers R_p with respect to the pure SAN (Fig. 9(a)). R_h and recoveries are less affected but LC1 concentrations of 7% and 10% reduce the recover depths for all scratch numbers. After 15 scratches under 5 N the 12.6% reduction in R_p is achieved with the addition of 10% LC1.

We now turn to PA6, the results are shown in Fig. 10. Asymptotes are seen for both penetration and recovery depths, for pure PA6 as well as for all lubricant-containing systems. The largest reductions in both R_p and R_h are seen for 7% LC1, so that further addition of the lubricant is counterproductive. As for the viscoelastic recovery, the highest ϕ values are seen in Fig. 10(c) for 1% lubricant.

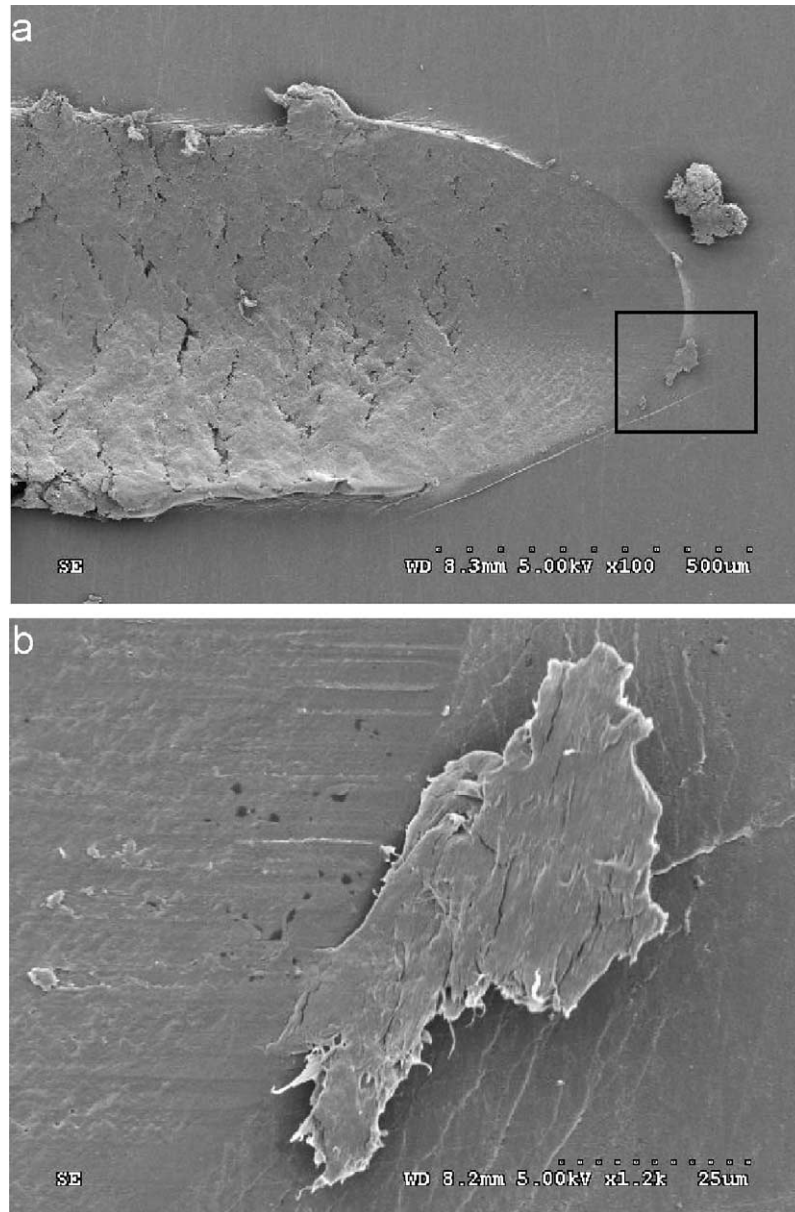


Fig. 15. Scratch track edge after 15 scratches under 10 N: (a) PS+1% LC1; (b) the same at larger magnification.

Thus, after 15 scratches, the maximum reductions in R_p (21.24%) and R_h (27.5%) are found for 7% LC1 while the maximum increment in recovery (7.9%) is seen for the material containing 1% LC1.

5. SEM results, scratching and wear mechanisms

Once again, we begin with polystyrene. Fig. 11 shows multiple scratch surfaces for PS + 1% LC1 as a function of the normal applied load. Extensive plastic deformation is observed under increasing loads, from 5 N (Fig. 11(a)), to

7.5 N (Fig. 11(b)) and 15 N (Fig. 11(c)), with increasing wear track width and massive wear debris under the maximum contact pressure for 15 N.

When we examine the effect of increasing LC1 concentration on PS under the constant load of 5 N (Fig. 12) a similar material removal mechanism is observed for PS (Fig. 12(a)) and PS+LC1 blends (Fig. 12(b)–(d)). However, increasing LC1 concentration gives rise to a more ductile behavior—with less crack nucleation.

Deformation mechanisms under constant load depend on the liquid crystal lubricant content. Fig. 13 shows the appearance of a crack edge for 1 wt% LC1 (Fig. 13(a)) and

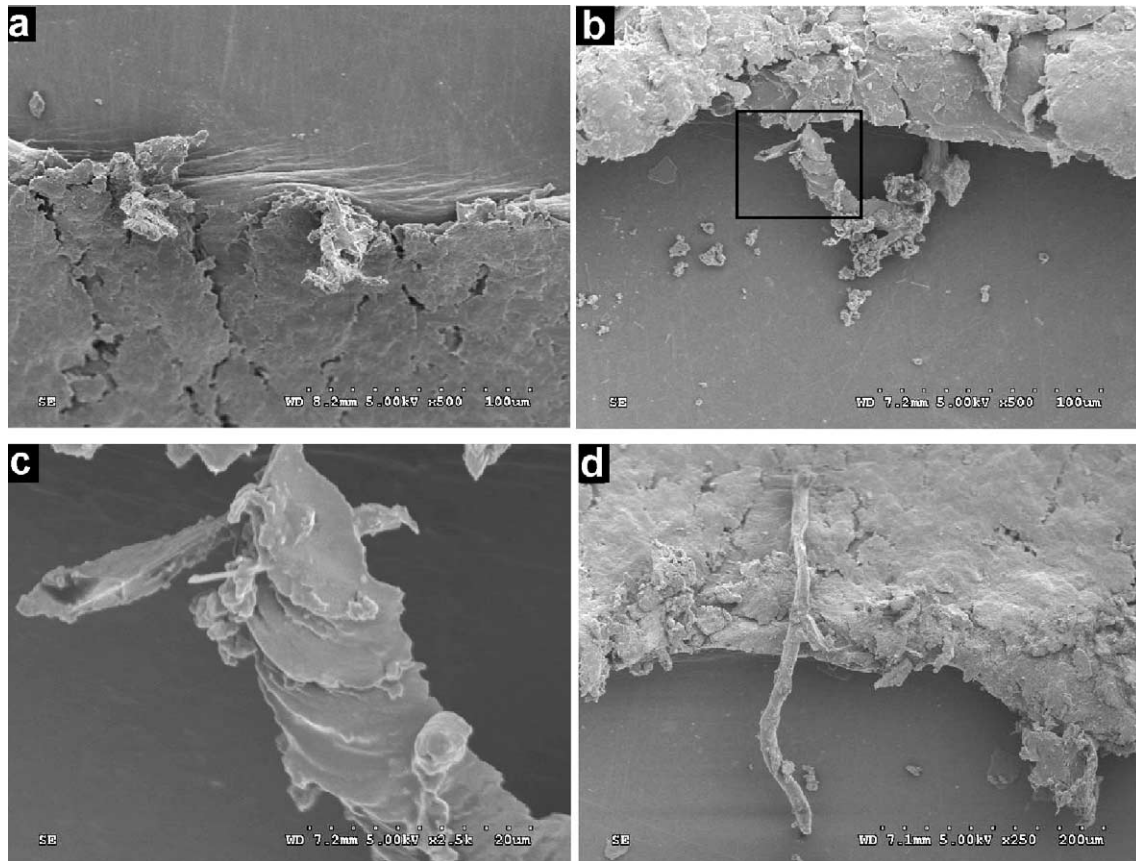


Fig. 16. SEM micrographs of PS + 3% LC1 under 12.5 N. (a) Scratch edge showing crazing. (b) Wear debris at the scratch edge. (c) Magnification ($\times 2500$) of wear debris formed by the adhesion of successive layers. (d) Wear debris morphology due to the rolling effect.

3% LC1 (Fig. 13 (b)) under 10 N. The material containing 1% of the lubricant (Fig. 13(a)) shows fragile behavior. Successive layers of deformed material accumulate at the edge—what leads to debris formation. By contrast, increasing LC1 to 3 wt% changes the deformation mode to more ductile. We observe a rounded morphology of the crack edges and the absence of wear debris (Fig. 13(b)).

To understand better mechanisms of crack growth with wear particle formation in PS, we have studied wear tracks under very mild conditions (2.5 N) for the highest LC1 concentration of 10%. Fig. 14 shows progressive magnifications of the wear track. We can observe the presence of parallel cracks, convex with respect to the sliding direction (Fig. 14 (a) and (b)), similar to those already seen by other authors [28–30]. Repeated passes finally produce particle detachment (Fig. 14(c)).

A different wear mechanism takes place under more severe conditions. Fig. 15 shows wear track and wear debris for PS + 3% LC1 under 12.5 N. Progressive magnifications from Fig. 15(a) to Fig. 15(b) show wear debris with the ‘chip’ morphology due to the machining effect of the indenter in the sliding direction. Fig. 16(a) shows a crazing

deformation mechanism at the edge of the wear track on PS + 3% LC1 under 12.5 N. Successive layers of plastically deformed material are observed for the same material in Fig. 16(b) and under a higher magnification in Fig. 16(c). We recall a thorough discussion of the crazing phenomena by Donald [31] including *craze breakdown* and *shear* as alternative types of behavior. Finally, fiber-like debris are formed (Fig. 16(d)) by the rolling effect of the indenter on the polymer surface.

Different wear particle morphologies are observed under the highest load of 15 N. Fig. 17(a) shows the flat shape of the particles trapped on the multiple scratch track, while Fig. 17(b) shows the more rounded morphology of those particles outside the contact path.

We have devoted so much space to polystyrene because of its brittleness—as reflected also in the absence of strain hardening unless a lubricant is present. We shall now consider the SEM evidence for the SAN copolymer; pertinent results are displayed in Fig. 18 for the pure material (a and b) and for SAN + 3% LC1 (c and d). The frontal view of the scar tip in Fig. 18(b) allows observation of successive layers of the deformed material after 15

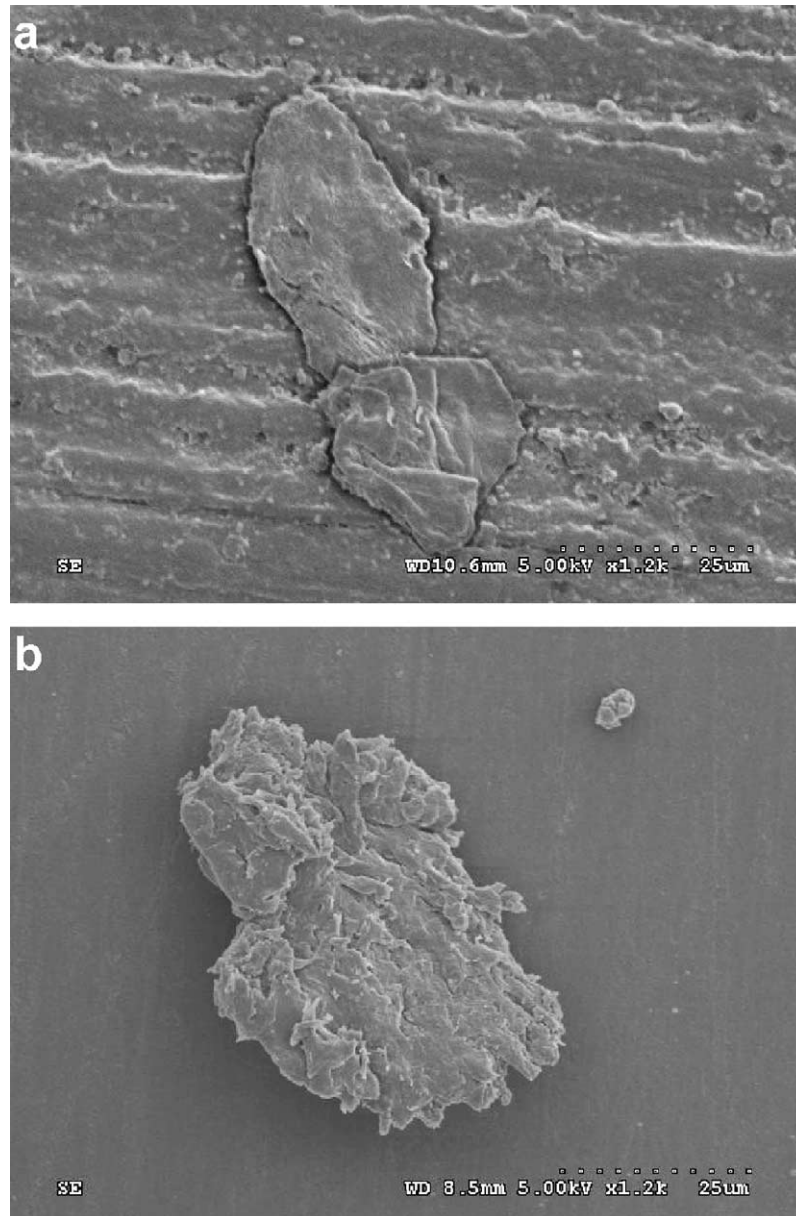


Fig. 17. Wear debris from PS+1% LC1 under 15 N. (a) Flat particle trapped on the scratching track. (b) Rounded particle outside the track.

scratches. Clearly, the debris accumulation is much less evident in the presence of the lubricant (Fig. 18(d)).

Selected SE micrographs for PA6 are shown in Fig. 19: pure polymer in Fig. 19(a) and PA6+3% LC1 in Fig. 19(b). Both show quite mild wear regimes with the elastic component of the deformation mode typical of PA, this even under the highest load of 15 N. No wear debris formation is observed in either system.

6. General discussion

We have shown before that strain hardening in sliding wear takes place in several polymers with a variety of chemical structures [19–21]. The only exception was polystyrene, but no lubricants were used in the studies just quoted. Against this background, the appearance of strain hardening in polystyrene now, after addition only 1 wt%

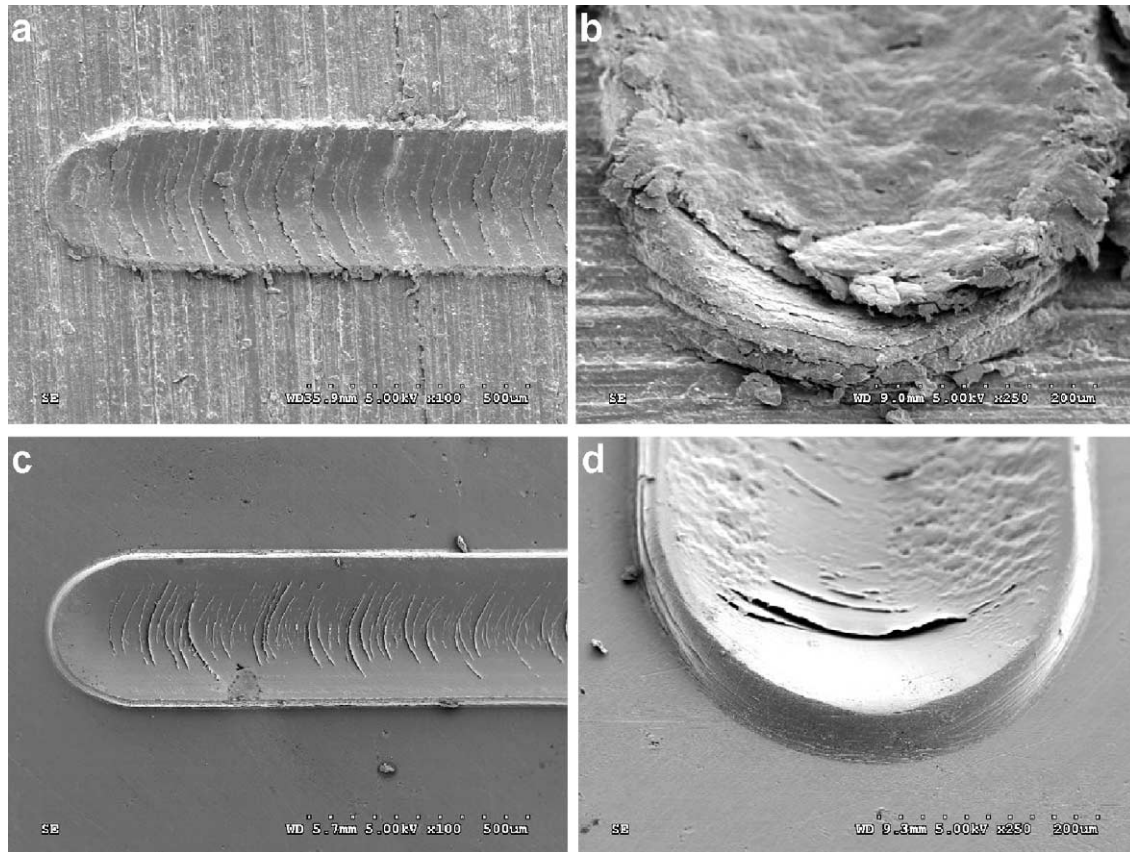


Fig. 18. SEM micrographs after 15 scratches: (a) SAN under 5 N; (b) SAN under 10 N; (c) SAN+3% LC1 under 5 N. (d) SAN+3% LC1 under 7.5 N.

of the monomer liquid crystal lubricant is significant. Apparently it is the presence of a non-ionic MLC lubricant which mitigates the brittleness of PS and brings this polymer in line with other polymers we have investigated.

Under low loads, PS and SAN based materials show plastic deformation with propagation of convex cracks parallel to the sliding direction. As normal load increases, track width increases while plastic deformation and material removal take place.

The main debris formation mechanisms in sliding wear are those of ploughing, crazing and machining. Flat rounded particles form when they remain trapped in the contact path while more irregular morphologies, including fiber-like particles produced by rolling, are observed outside the scratch track.

While liquid lubricants can be used to lower friction—and thus wear—of moving metal parts without problems, this approach cannot be universally used for polymers. As mentioned in Section 1, polymers can swell under the influence of a liquid or a dissolved vapor; this effect is well known in elastomers [32]. Therefore, liquid lubricants for polymers constitute a two-edged sword—the main reason

why solid lubricants such as MoS_2 are in use. However, as reported in [13] and also found here, MoS_2 can cause an *increase* of friction. For Polyamide 6 both static and dynamic friction have increased after addition of MoS_2 . By contrast, we have demonstrated above that a judicious choice of liquid lubricants to achieve both friction lowering and higher scratch resistance is possible.

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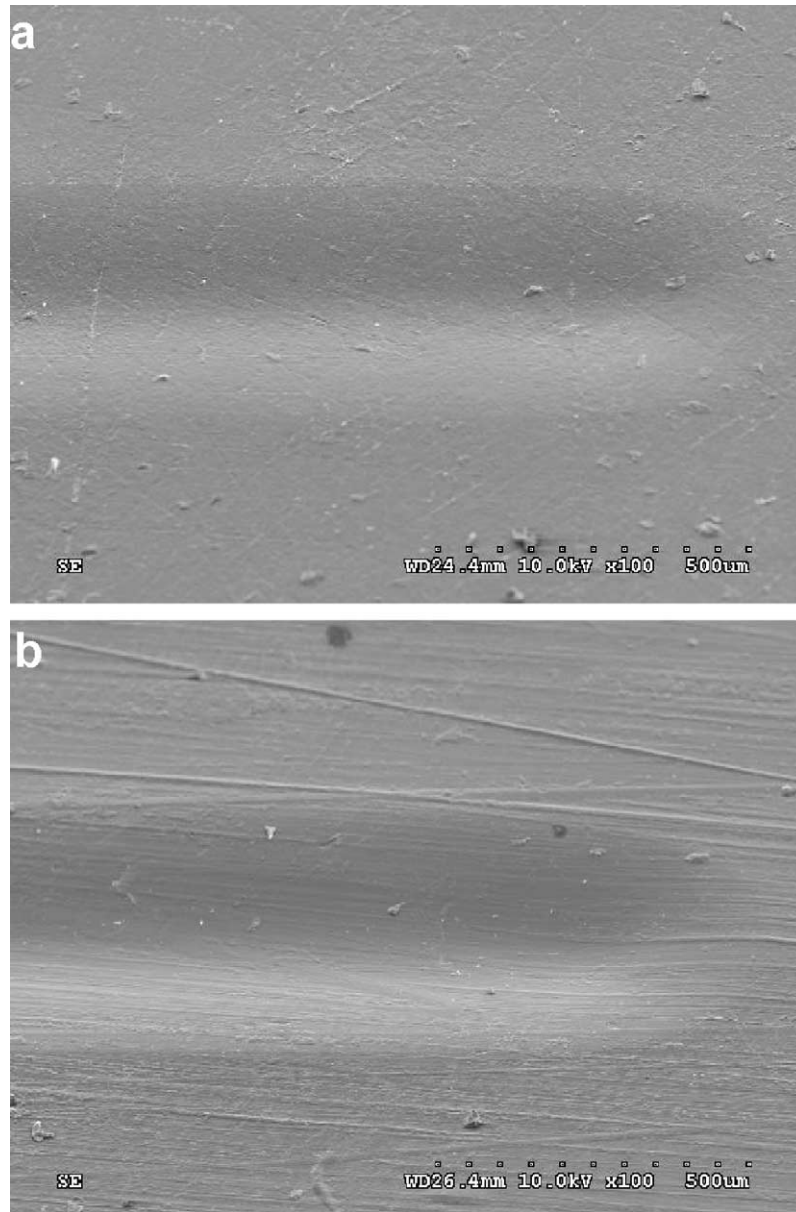


Fig. 19. SEM micrographs after 15 scratches under 15 N: (a) PA6; PA6+1% LC1.

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