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A study of the abrasive wear in the polishing of polypropylene using X-ray photoelectron spectroscopy

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The study of the abrasive wear of polymers is important both in the preparation of polymers prior to joining and in the techniques used to expose surfaces and interfaces for examination by a variety of analytical methods. In this investigation by X-ray photoelectron spectroscopy, the influence of the atmosphere on the chemical damage to polypropylene during the process of abrasion was examined, looking in particular for evidence of surface oxidation. The extent to which particles of abrasive, alumina in the present case, are introduced into the polymer was also examined. In this case a comparison of dry and lubricated polishing was made. The latter was found to be the more damaging, with damage increasing in relation to the solubility parameter of the solvent (lubricant). The work has shown that the simple cutting of the surface by an uncontaminated knife is the cleanest method for the exposure of the internal surfaces of the polymer. No advantage is gained by shaving the surface in argon or vacuum over that produced by shaving in air. Dry abrasion using alumina is effective in removing pre-existing contamination, but significant quantities of alumina are introduced into the surface. One effect of this is to produce a large oxygen signal that would make subsequent analytical interpretation difficult. As indicated above, lubricated abrasion seems quite unacceptable.

1. Introduction

Abrasive wear of polymers occurs when the surface is cut or scratched with sharp protuberances. The abrasive wear develops during friction of rigid plastics on the surface of an abrasive cloth, in which case the wear process is related to the cutting and ploughing of the surface by the abrasive cloth granules [1].

Among other factors, abrasive wear depends to a great extent on the environment, the initial state of the polymeric surface, the moisture content and the lubrication [1]. Because the abrasive wear is essentially confined to the polymeric surface, delineation of the initial interaction of a polymeric system with the abrasive requires a knowledge of the physico-chemical structure changes, probably in the outermost few micrometres of the sample. Although the monitoring of changes in bulk chemistry and mechanical properties as a function of the abrasive wear has been the subject of numerous studies, changes in the surface region have not been the object of similar efforts.

The study of the structure, bonding and reactivity of the outermost surfaces of polymeric systems has been facilitated by the development of electron spectroscopy (XPS). The results described below demonstrate that XPS as technique provides considerable new insight into the critical stages of abrasion of polymers in terms of the quantity of contamination at the very surface.

In this investigation we have examined the influence of the atmosphere on the chemical damage to the polymer during the process of abrasion, looking in particular for evidence of oxygen (water, O_2) uptake by the freshly exposed surface. The work has relevance to the practice of surface preparation prior to joining engineering sections manufactured in polymer by welding. The findings are also relevant to the characterization of the original surface contamination of polymeric materials and the way of eliminating this contamination. Finally, the findings are relevant to our own interests in the techniques available for exposing interfaces within coated sections by use of abrasion.

2. Experimental procedure

The material used for this investigation was polypropylene sheet prepared in our laboratory by injection moulding and had a stabilizer content of about 0.9% (of unknown composition). It was cut with a saw, trying to introduce as little contamination as

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possible, into square samples of area 1 cm^2, and thickness 1 mm. These samples were suitable for examination in the XPS spectrometer (VG Scientific, ESCA 3 MkII). In the initial part of the investigation, samples were shaved using a hardened steel blade produced for the purpose. A commercial blade such as a razor blade or scalpel was not considered suitable because of the possibility that the cutting edge would be coated or lubricated and thus introduce a source of contamination. For the experiments in which the surface was shaved in vacuum the blade was attached directly to a "wobblestick" allowing operation inside the preparation chamber of the instrument.

The X-ray photoelectron spectra were recorded using aluminium radiation with a pass energy of 50 eV (survey scan) or 20 eV (individual regions), giving a resolution (full width at half maximum) of ~ 1 eV. The vacuum in the analyser chamber was about 5×10^{-8} torr (1 torr = 133.322 Pa). Data acquisition and data treatment were controlled via a V. G. 3040 data system based on a computer DEC PDP 8e. For each sample, a general spectrum was recorded (1200 eV) and also a high-resolution spectrum (20 eV) was obtained for each of the elements present. The surface atomic concentration was calculated using the intensities of the spectral peaks and the atomic factors reported for those levels [2].

The peak shapes of carbon, oxygen, aluminium, sodium and silicon were studied for each sample during the course of the investigation, but this was found to remain unchanged and hence conveyed little information. Representative spectra are shown in Figs 1 and 2. The major variation in the results from XPS spectra were mainly related to the change in atomic concentration of the main contaminants such as oxygen, aluminium and sodium, as polishing time increased (from 1–20 min).

The standard conditions used for this investigation were: (a) air admitted from the laboratory into the preparation chamber of the XPS to a pressure of 1 atm; (b) argon, in the preparation chamber, also at a pressure of 1 atm; and (c) vacuum, at the normal operation pressure of the spectrometer, 10^{-8} torr.

In the second part of the investigation, samples were polished with dry alumina in air or in argon. Alternatively, samples were polished with a mixture of alumina and organic solvents as listed in Table I. Alumina polishing medium (1 μm) was rubbed, as a dry powder, into the nap of a metallurgical polishing cloth supported on a glass square. The polypropylene samples were rubbed with an oscillatory motion against this surface for 1, 5, 10 and 20 min. In examining lubricated abrasion, the solvents were periodically run on to the cloth from a pipette. Polishing samples in an argon atmosphere required the use of glovebox, but the gloves themselves proved to be inadequate protection against contamination. Simply the touch of the plastic gloves produced a dramatic change in the oxygen content of the sample (Fig. 1) and thus it was necessary to use a sample holder to provide isolation between the sample and the gloves. Because of the gloves and sample holder, less force could be applied to the sample and abrasive wear was less than when polishing in air. Thus, after the work of polishing in argon, a new comparative experiment was made using air within the glovebox.

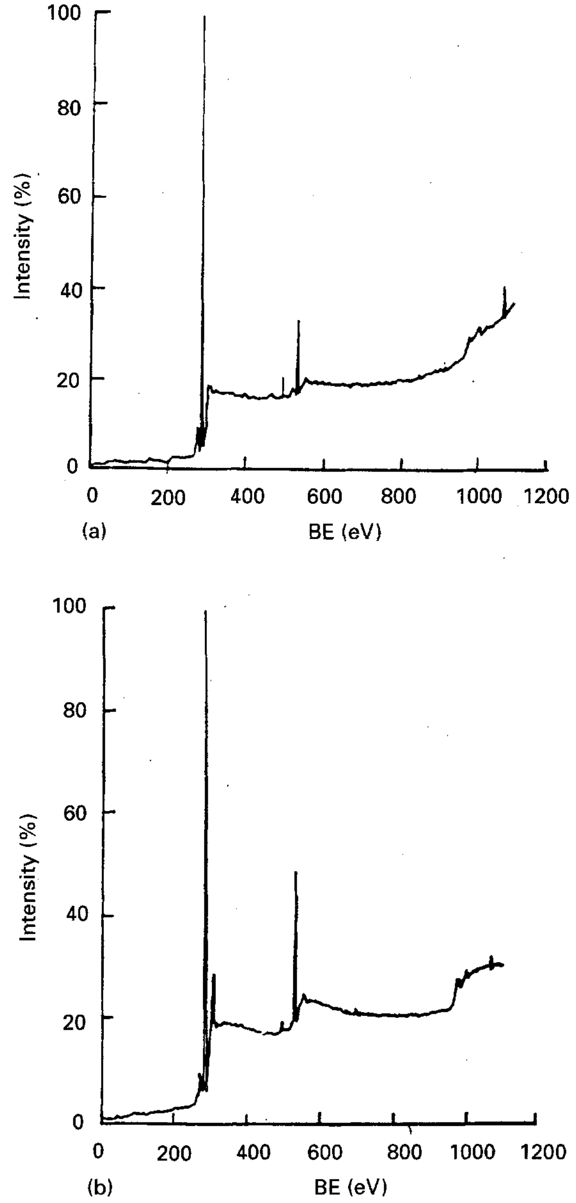

Figure 1 Spectra from the surface of polypropylene: (a) normal specimen, (b) same specimen exhibiting a high increase in oxygen content after touching with a plastic glove.

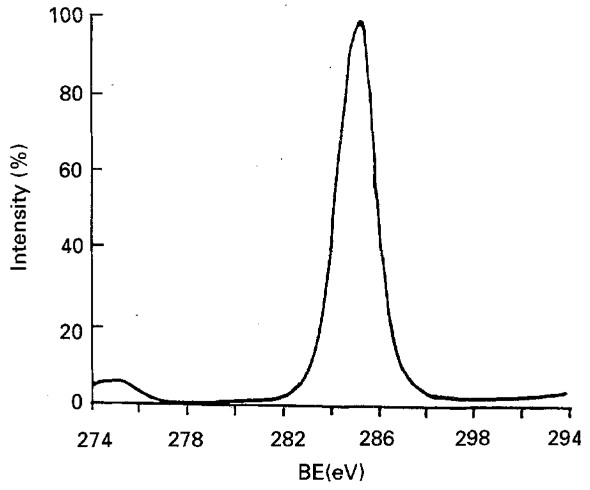

Figure 2 C 1s spectra for the polypropylene.

TABLE I List of solvents used as lubricants

Acetone (CH_3COCH_3)
Methanol (CH_3OH)
Carbon tetrachloride (CL_4C)
Trichloroethylene (Cl_2CCHCl)
Chloroform ($CHCl_3$)
Toluene ($C_6H_5CH_3$)

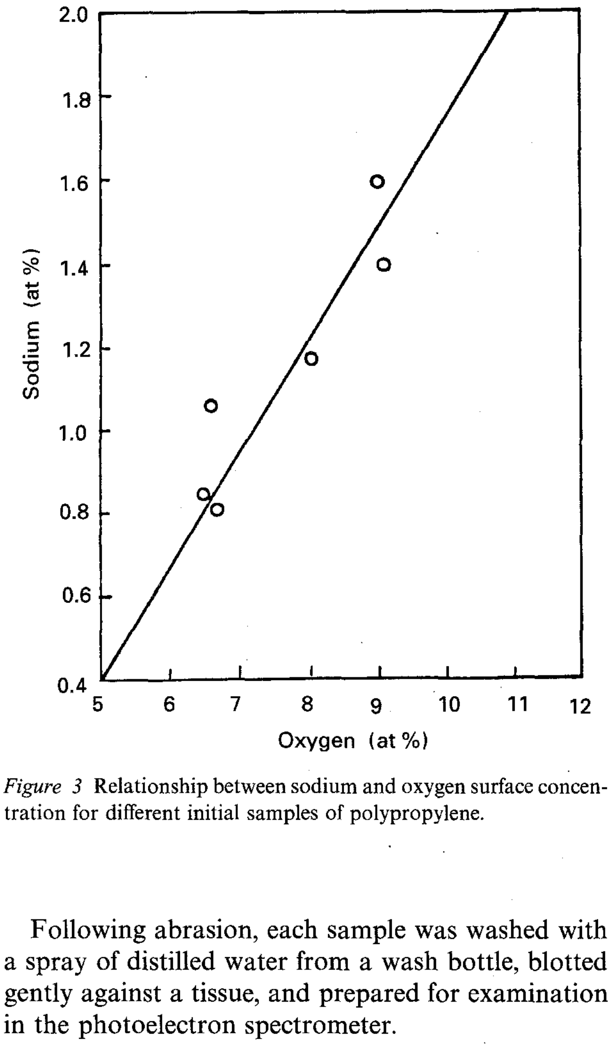

Figure 3 Relationship between sodium and oxygen surface concentration for different initial samples of polypropylene.

Following abrasion, each sample was washed with a spray of distilled water from a wash bottle, blotted gently against a tissue, and prepared for examination in the photoelectron spectrometer.

3. Results and discussion

3.1. The initial state of the polymer and the production of clean surfaces

In the first instance, a series of spectra were recorded to determine the atomic composition of the initial surface in its "as-delivered" form. These showed that the sample surface was contaminated by oxygen, as the main impurity, and small quantities of silicon and sodium. The moulded surface of the polypropylene was very bright and it seems probable that the surface contamination was associated with the mould-release treatment. The sodium (BE 1072.4 eV) was related to the oxygen in a ratio close to O/Na = 3.75. Fig. 3 shows the data for a number of samples on which this estimate was based. The sample was washed with a spray of distilled water and with acetone from a wash bottle and blotted gently against a tissue, but the signal from sodium and oxygen did not disappear. Traces of sodium in the polymer have been also observed in other studies, as for polyvinyl alcohol [3].

In our experiments, about 1 at % silicon (BE 102.4 eV) was observed on the polypropylene surface. Briggs [4] detected silicone on the surface of low-density polyethylene (LDPE), probably of the type used as a mould-release agent, which is a stress corrosion agent for LDPE. On a study of the adhesion of CrO_3–H_2O etched LDPE to an epoxide adhesive, Briggs *et al.* [5] also observed small peaks due to silicon with a negative effect for adhesion values. In addition, Briggs *et al.* [6] detected silicon contamination on a non-woven polypropylene fibre product. Chang and Thomas [7] observed the presence of silicon and oxygen in an unpurified film of PVC, which resulted in a fast photo-dehydrochlorination when exposed to MgK_α X-rays.

When samples were shaved with a scalpel in argon, vacuum or air, the contaminated surface was easily removed. Comparative spectra from these treatments are given in Fig. 4, which should be compared with Fig. 1. The disappearance of the surface layer is associated with the loss of oxygen, sodium and silicon peaks from the XPS spectra. No difference could be found between the procedures of shaving in air, argon or vacuum as far as the spectra were concerned (Fig. 4). Visually, the generation of a matt finish on the shaved sample is observed.

Further experiments were conducted showing that the sample did not become more sensitive to atmospheric contamination after eliminating the outermost contaminated surface layer. Moreover, a sample was cleaned by vacuum shaving for 10 min, and then exposed to air for 30 min without there being any trace of oxygen uptake. The survey spectra for these samples are given in Fig. 5. The behaviour appears to be different from that observed with commercially produced low-density polyethylene, which exhibits substantial signals corresponding to water absorption [8].

3.2. Study of the abrasive wear

3.2.1. Abrasion in air

Samples were examined after intervals of 1, 5, 10 and 20 min. After only 1 min the outermost sodium contamination has been completely removed and the oxygen reduced to about 25% of its original value (Fig. 6). After this first step, the effect of polishing for longer times was to change the quantity of alumina introduced in the polymer, with a trend to introduce more alumina at longer times of polishing (Fig. 7). The fact that the alumina is the principal source of the very prominent oxygen peak is seen from the plot of oxygen against aluminium concentration for abrasive wear in air, which is a line, with a coefficient of correlation of about 0.98, passing through the origin (Fig. 8). The slope gives an Al/O atomic ratio of 0.27, which is much lower than expected. However, a separate measurement showed that the alumina used in this work had an average ratio Al/O = 0.37, suggesting that some water had been absorbed by the alumina. In confirmation of this, the oxygen spectrum showed a single peak at 533.5 eV, in accord with the presence

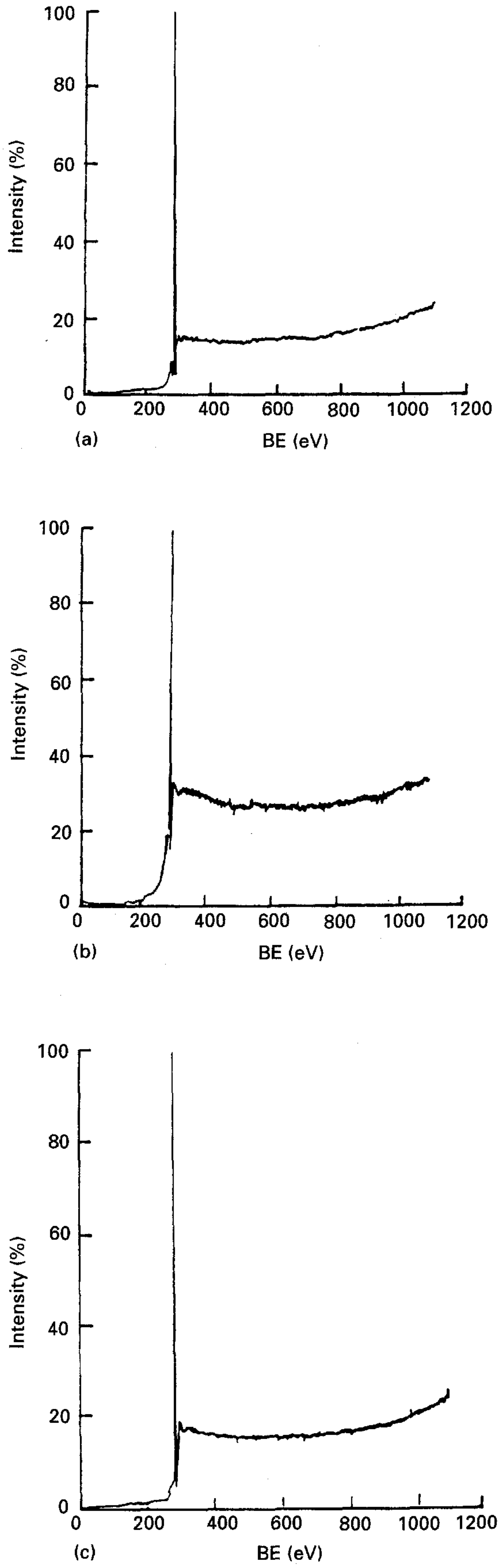

Figure 4 Spectra from the surface of polypropylene after shaving inside the preparation chamber in different atmospheres: (a) in air, (b) in vacuum, (c) in argon.

of oxygen as the hydroxyl ion. The increasing aluminium content with time was related with a higher quantity of deposited alumina in the polypropylene surface produced by the longer polishing time.

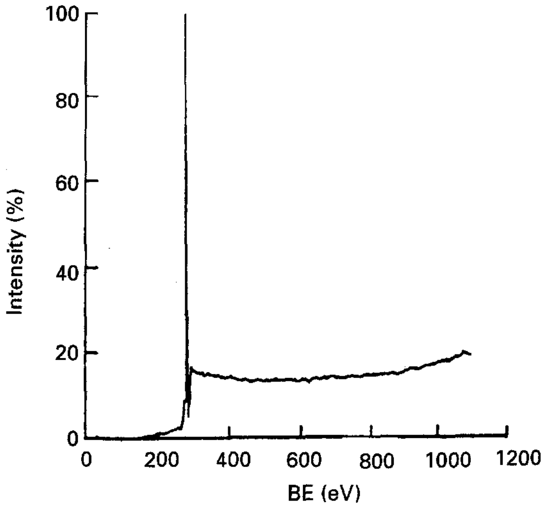

Figure 5 Spectra from the surface of polypropylene after shaving in argon and exposure to the atmosphere for 30 min.

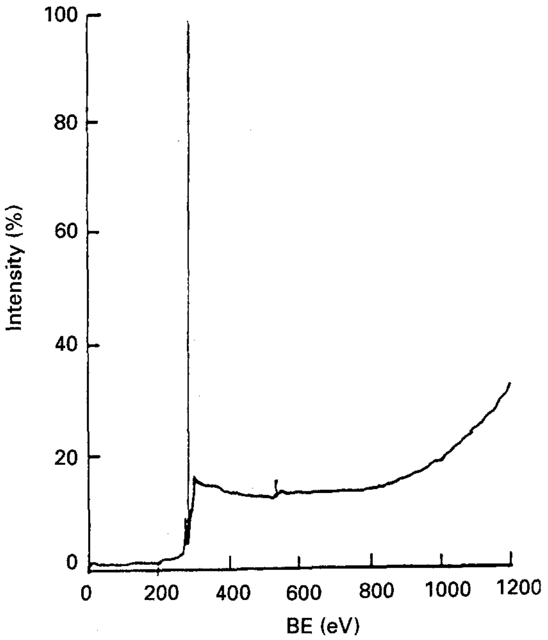

Figure 6 Spectra from the surface of polypropylene after polishing in alumina for 1 min.

3.2.2. Abrasion in argon

The environment plays a fundamental role in the physicochemical processes that take place on friction and wear of metallic surfaces. For rigid polymers, however, environmental effects have still not been adequately studied. According to data mentioned by Bartenev and Lavrentev [1], atmospheric oxygen seems to be the most active environmental agent, hence the interest in avoiding its effect using an inert gas.

A polishing time of about 10 min in an argon atmosphere was required to obtain the minimum oxygen concentration and to remove sodium when the glovebox was used. As seen in Fig. 9, the evolution of oxygen and sodium with polishing time was independent of the presence of air or argon within the glovebox. A minimum in both oxygen and aluminium is found at 10 min, but prolonged polishing leads to a marked increase in alumina contamination of the

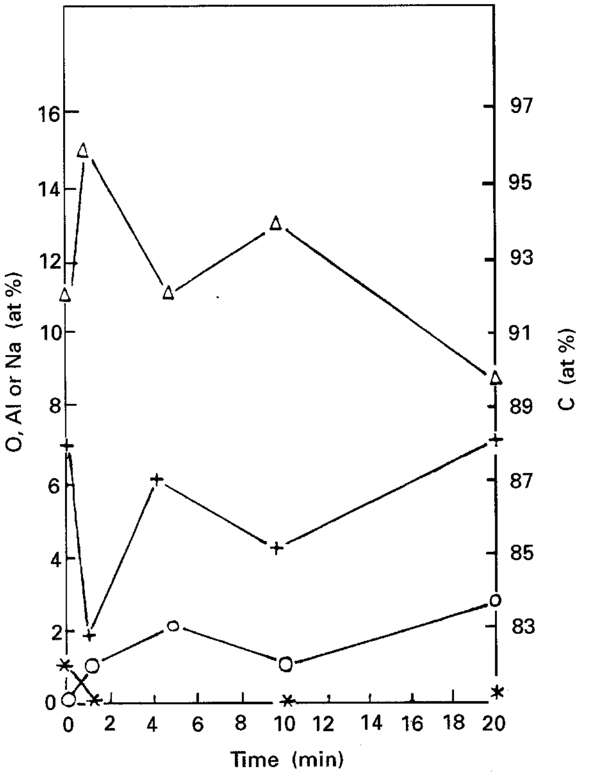

Figure 7 Atomic surface concentration as a function of time of direct polishing with alumina. (△) Carbon (+) oxygen, (○) aluminium, (*) sodium.

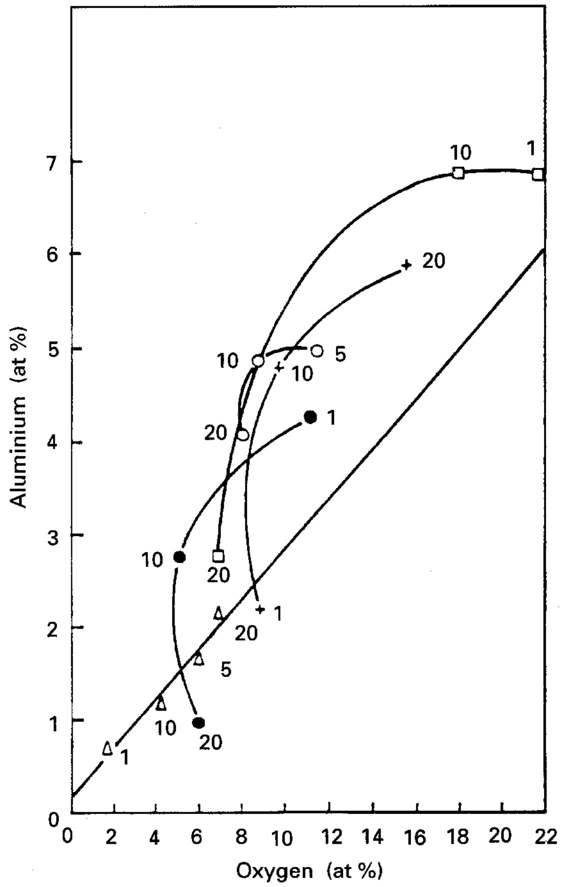

Figure 8 Relationship between aluminium and oxygen surface concentration under different times (in min beside each point) and conditions of polishing in (△) air, (+) carbon tetrachloride, (□) trichloroethylene, (●) methanol, (○) toluene.

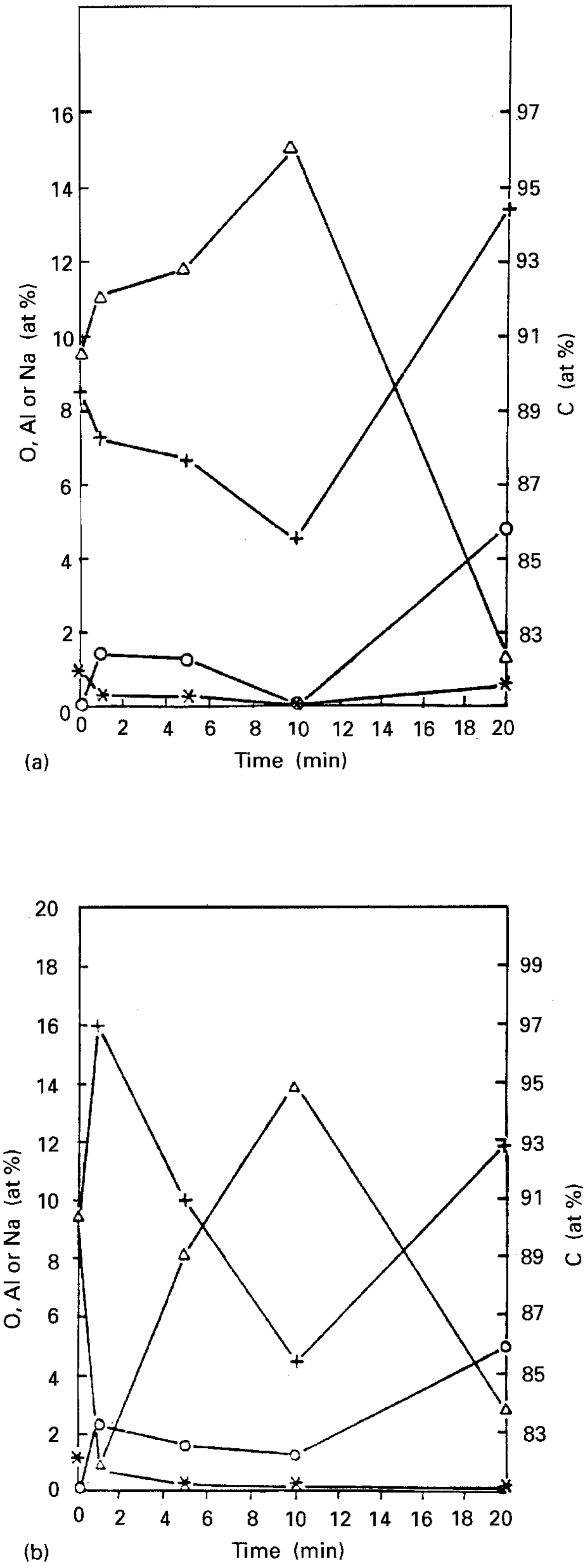

Figure 9 Atomic surface concentration as a function of time of polishing in different atmospheres inside the glovebox: (a) in air; (b) in argon. (△) Carbon, (+) oxygen, (○) aluminium, (*) sodium.

surface. The similarity in behaviour between air and argon shows that there is unlikely to be an oxidative component on the polymer surface.

It is interesting to point out that the required polishing time to reach the minimum concentration in Fig. 9 is ten times greater than that for direct polishing without the use of the glovebox (Fig. 7). This result is consistent with the fact that polymer wear resistance is

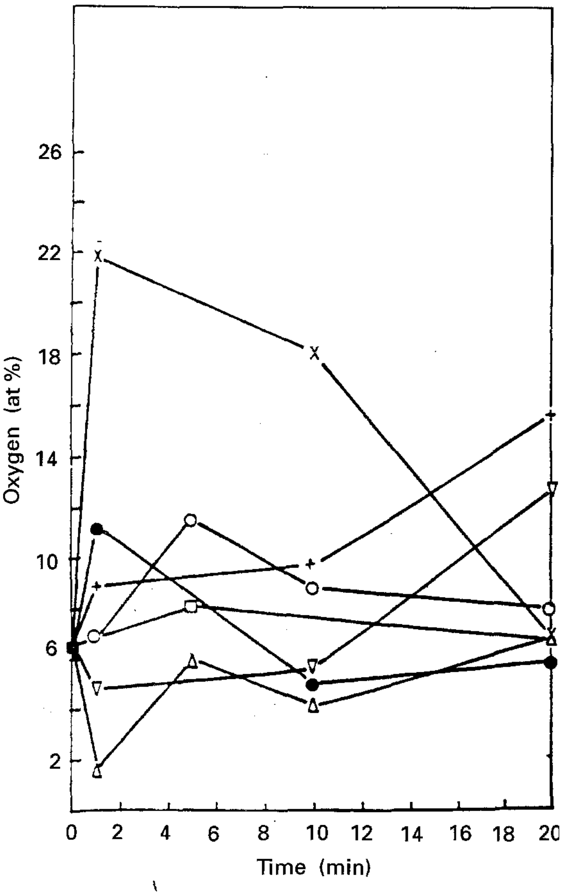

Figure 10 Oxygen surface concentration as a function of time and lubricants used during polishing: (△) alumina (unlubricated), (▽) acetone, (+) carbon tetrachloride, (×) trichloroethylene, (□) chloroform, (●) methanol, (○) toluene.

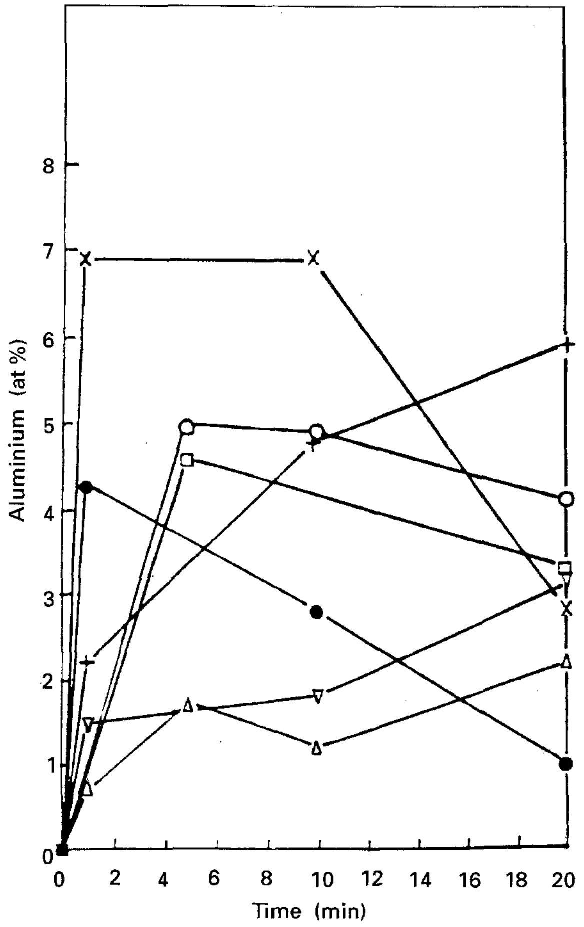

Figure 11 Aluminium surface concentration as a function of time and lubricants used during polishing: (△) alumina (unlubricated), (▽) acetone, (+) carbon tetrachloride, (×) trichloroethylene, (□) chloroform, (●) methanol, (○) toluene.

proportional to pressure [9, 10], and this was less inside the glovebox.

3.2.3. *Lubricated abrasion*

The anticipated trend for lubricated abrasion is for high levels of contamination, and hence several possible organic solvents were compared. It is reasonable that the abrasion process may be influenced by the interaction between solvent and polymer. With regard to this, it is reported that polypropylene shows extensive swelling in contact with polar organic solvents at room temperature; e.g. carbon tetrachloride gives 169 ml swelling agent adsorbed on 1000 ml polypropylene at room temperature [11]. There is also the possibility of an effect of the alumina on the lubricant absorption in the same way that deposition of tin and iron hydrous oxides on a polyethylene surface renders this surface wettable [12].

The fluids used as lubricants are given in Table I. Note that only acetone and methanol contained oxygen groups that might increase the oxygen atomic concentration on the polymer surface. This is relevant because the change in concentration of oxygen with time is totally different to that found with unlubricated abrasion. Both the oxygen and aluminium content increased on the polymeric surface from the earliest time of polishing and reached a maximum after short times, Figs 10 and 11. The uptake of oxygen is particularly marked and the Al/O atomic ratio was bigger than found in unlubricated abrasion. Notwithstanding this rapid uptake of abrasive, the surface remained bright and polished after even the longest polishing period (20 min). An interesting feature (Figs 10 and 11) is that alumina uptake eventually decreases with polishing time and the values for practically all lubricants converges to those found for unlubricated polishing. After polishing for 1 min, for all lubricants, the sodium peak disappeared from the polymeric surface composition. The C 1s spectra for the polymeric surfaces resulting from polishing with lubricants did not show peaks that could be assigned to C–Cl, C–OH or C=O carbon species associated with the lubricants used. The absence of these components and the chlorine peak in the general XPS spectra of the polymeric surfaces polished with chlorinated lubricants, confirms the absence of significant lubricant residue on the polymeric surface.

The results in Figs 10 and 11 show that the level of contamination with alumina on the polypropylene surface increased in the order: acetone < methanol < chloroform < carbon tetrachloride = toluene < trichloroethylene. It is interesting to note that the levels of contamination with alumina range in the same order of the reported [11] volumes of swelling on polypropylene at room temperature by those lubricants (there is no information for trichloroethylene).

The absorption of lubricants by the outer polymeric surface must be a relatively fast process because, practically, in all the lubricants, the amount of oxygen and aluminium reaches a maximum after only 1–5 min. The absence of the characteristic groups of the lubricants in the high-resolution spectra indicates that the absorbed lubricant might be quickly desorbed, yielding solid alumina in the polymeric surface. Furthermore, the incorporation of the alumina into plastic surfaces might lead to considerable changes in water/polymer contact angles, as was found with iron oxides in PTFE [13]. This might open the possibility for further contamination of the plastics by water. Surely for this reason, the [O]/[Al] atomic ratios we have obtained are larger than those for polishing without lubricants (Fig. 7).

At longer polishing times (about 20 min, Figs 10 and 11) the trend to decrease the aluminium and oxygen atomic content suggests that the adherent deposits of alumina in polypropylene might be removed by abrasion, which probably removes oxide together with polypropylene.

4. Conclusion

Based on the aforementioned results, lubricated polishing appears to be particularly damaging to the polymer surface, rapidly adding a transfer film of alumina and possibly molecules of polymer released by the swelling process. It takes much longer for the same process to occur in unlubricated polishing. Brief polishing (1 min) with dry alumina is effective in removing traces of release agent and other surface contamination without introducing severe alumina contamination. Unlubricated polishing is ineffective in removing significant amounts of polymer and could not be used for mechanical depth profiling to expose interfaces. The only effective method seems to be that of shaving with a knife and, crude though this is, a single cut with a scalpel at a shallow glancing angle through an interface would be the preferred method. When a lubricant is essential, for example as a carrier for the abrasive in ball cratering, then acetone seems to be the best choice. The order of damage increases with solvent in an order which appears to be that of the solubility parameter for the liquid/polymer interaction.

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