

*Comments on "X-ray photoelectron spectroscopy studies of polymer surfaces Part 2 Melting polyethylene against aluminium".*

It was with considerable interest that we read the recent paper by Briggs, Brewis and Konieczko on an ESCA (XPS) investigation of samples of polyethylene prepared by melting against aluminium foil [1]. Unfortunately although the work essentially duplicates work published from these laboratories several years ago [2] it would appear that some of the conclusions conflict with our prior study, which was of somewhat different emphasis. It is the purpose of the short communication to point out that the results presented in both papers [1, 2] are entirely reconcilable and that in drawing a comparison with our own work Briggs and coworkers have misrepresented the situation since there are real differences in the two investigations the subtlety of which was clearly not appreciated by these authors in drafting their manuscript.

At the outset it is clear that the validity of any comparisons between the two studies rests on the comparability of the sample preparation. In this respect there are three major differences. (1) The samples of high-density polyethylene prepared in our work were hot pressed under three different conditions using degreased annealed aluminium foil as the pressing matrix. Since we have previously shown that the hydrocarbon contamination present on commercially fabricated aluminium is tenaciously held almost certainly in the form of an aluminate soap [3] the net effect of the degreasing procedure is to remove relatively low molecular weight hydrocarbon contamination leaving a composite surface/subsurface of aluminate soap, aluminium metal. By contrast Briggs and coworkers use a Chromic acid etch on the aluminium foil and since incomplete data were presented it is not clear that the chemical compositions of the initial pressing surface have been characterized. (2) Whilst our work was essentially devoted to the surface oxidation of pressed films produced at  $\sim 200^\circ\text{C}$  by press-

ing in (i) air, (ii) in a nitrogen atmosphere and (iii) in an argon atmosphere after several cycles of pump down and exposure to argon to remove entrained oxygen [2], Briggs and coworkers have focussed attention on films pressed solely in air at somewhat lower temperatures ( $150$  to  $175^\circ\text{C}$ ). (3) Whilst the main interest of our work was the production of oxygen-free films of high-density polyethylene with an ancillary investigation of the cohesive failure close to the polymer/foil interface, Briggs and coworkers have had the somewhat complementary objective of looking at the surface produced at the interface of the polymer/foil by dissolution of the metal/metal oxide component in dilute sodium hydroxide solution\*. It should be evident from this that, although the two investigations have features in common, direct comparison without due allowance for the differences in emphasis and sample could and in fact does lead to erroneous conclusions if due care and attention are not exercised.

It is pertinent at this point to briefly summarize the results presented in our previous paper [2] so that comparison may directly be drawn with the work of Briggs and coworkers [1]. By studying the surfaces of the peeled samples of high-density polyethylene the following conclusions were reached.

(i) In peeling the polymer samples from the pressing matrix, cohesive failure leaves in all cases  $\sim 2$  monolayers or so of polymeric material adhering to the foil. Briggs and coworkers have apparently rediscovered the same effect.

(ii) Samples pressed in air showed extensive oxidation as evidenced by both the  $\text{O}_{1s}$  and  $\text{C}_{1s}$  levels and indeed we have pointed out that such oxidation extends well into the bulk, since functional groups are detected by bulk techniques such as transmission infra-red and multiple attenuated total internal reflectance. Apparently this result has also been rediscovered by Briggs and coworkers the only new information being provided being the entirely reasonable one that oxidation is somewhat less if films are pressed at a lower temperature.

\*It is not clear that such treatments provide uncontaminated surfaces since the carboxylic acid material in the aluminate soap may still be retained at the surface, and indeed the convolution of thermodynamic and kinetic factors involved in the dissolution process make it by no means certain that all of the aluminium is removed. Briggs and coworkers mention that no signals were detected corresponding to photoemission from Al core levels in the samples prepared in this way, but back of the envelope type calculations reveal that sub-monolayer coverage would probably have gone undetected being some two orders of magnitude or so lower in signal intensity.

(iii) For the polymer surfaces prepared by pressing under the three separate conditions described in our earlier work, it was shown that, in contrast to the extended nature of the oxidation for films pressed in air, films pressed in a nitrogen atmosphere exhibited relatively low levels of oxidation, whilst those prepared by specifically excluding oxygen by successively cycling in an argon atmosphere exhibited no oxidation. From the  $O_{1s}$  to  $C_{1s}$  peak are ratios and the overall band profile for the  $C_{1s}$  levels of the sample prepared by pressing in nitrogen, it was inferred that these samples exhibited submonolayer levels of oxidation. Briggs and coworkers claim to have disproved this, although the basis of their argument is extremely tenuous, since their experiments as we have previously noted do not correspond to those reported previously from these laboratories. To emphasize this point it may be noted that the surface nature of the oxidation for these peeled films is readily demonstrated by recourse to angle-dependent studies. Thus Fig. 1 shows the angle-dependent  $C_{1s}$  and  $O_{1s}$  core level spectra for samples which are somewhat more extensively oxidized than those actually used in our surface fluorination paper.\* In going from a take-off angle of  $35^\circ$  to  $70^\circ$  with respect to the normal to the sample surface the  $O_{1s}/C_{1s}$  intensity ratio changes by  $\sim 35\%$  clearly indicating that the oxygen functionality is confined to the surface regions. With a knowledge of electron mean free paths<sup>†</sup> and of the relative cross-sections for photo-ionization from the two core levels the data may be quantitatively described if oxidation extends over two monolayers with the extent of oxidation being  $\sim 1$  carbon atom in five. Since this sample is more extensively oxidized than those originally employed as evidenced by the overall  $C_{1s}/O_{1s}$  intensity ratios the original estimate that the oxidation in the peeled samples of films prepared by pressing in nitrogen (as used in the surface fluorination work) is confined to the first monolayer is entirely consistent. The fine structure of the  $C_{1s}$  levels reinforces this conclusion. Thus on the basis of the considerably larger mean free path for electrons photo-emitted from the  $C_{1s}$  levels as

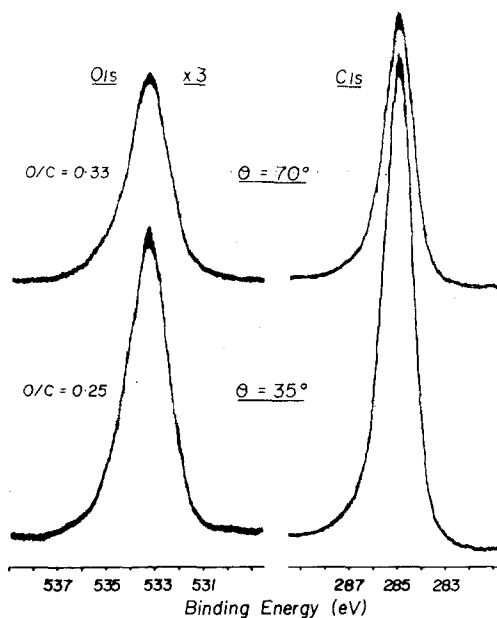


Figure 1  $O_{1s}$  and  $C_{1s}$  core level spectra, for polyethylene pressed under a nitrogen atmosphere, recorded at electron take-off angles of  $35^\circ$  and  $70^\circ$ .

compared with the  $O_{1s}$  levels [4] it is a straightforward matter to accommodate the fact that, despite the relatively intense  $O_{1s}$  signal arising from carbonyl features, the  $C_{1s}$  spectra themselves show relatively little evidence for  $>C=O$  structural features. It should be emphasized however that these observations are only explicable in terms of oxidation (in the peeled films prepared by our method (ii)), being confined to the surface of the samples. By contrast the peeled samples prepared by Briggs and coworkers obviously exhibit oxidation into the subsurface and bulk as may readily be appreciated from a comparison of the  $C_{1s}$  levels for the aluminium foil subsequent to peeling off the polymer film. The  $C_{1s}$  levels exhibit extensive fine structure attributable to both  $>C=O$  and



own findings on samples prepared by pressing in air. The work reported by Briggs and coworkers in no way disproves our earlier claim therefore

\*These samples were some of the first to be prepared by pressing under a nitrogen atmosphere and since they were too extensively oxidized to be used in the surface fluorination experiments described several years ago, still happened to be available.

<sup>†</sup>The mean free path in a typical polymer of electrons photoemitted from a carbon  $1s$  core level, by  $MgK\alpha_{1,2}$  radiation has recently been directly determined to be  $\sim 14 \text{ \AA}$ .

concerning the extent of oxidation in peeled films of high-density polyethylene prepared by pressing in a nitrogen atmosphere.

There are two further comments which should be made concerning the work by Briggs and co-workers which may avoid confusion in any subsequent study. First it is known that *lightly contacting* polymer films of different triboelectric properties leads to mass transfer between the two components [5]. If polymer films are *prepared* well above their  $T_g$ s the outcome is by no means clear cut and it therefore seems doubtful that the situation is as straightforward as Briggs and co-workers imply. Secondly the claim has been made that unsaturation may be determined by investigation of the relative intensity ratios of  $C_{1s}/Br_{3d}$  levels after short immersion of samples in bromine in carbon tetrachloride solution. There are three major objections to the simplistic view implicit in the paper by Briggs and co-workers in this connection. Firstly a considerable amount of data has been accumulated on the kinetics and mechanism of bromination of alkenes and it is by no means clear that allylic bromination would not form a substantial part of the overall reaction since the concentration of bromine at the very interface might be quite low [6]. Secondly since the activation energy for the addition reaction is not inconsiderable and since the reaction is carried out in solution it is not inconceivable that there could be substantially different rates of overall reaction for crystalline and amorphous regions. Since angular dependent studies were not reported it is

not possible to ascertain whether the brominated samples were both laterally and vertically inhomogeneous. Finally the possibility of adsorption of bromine containing species (e.g. HBr) at the surface cannot be discounted since our own work has shown that desorption of such species is often slow particularly if hydrogen bond formation is involved [2, 7].

## References

1. D. BRIGGS, D. M. BREWIS and M. B. KONIECZKO, *J. Mater. Sci.* **12** (1977) 429.
2. D. T. CLARK, W. J. FEAST, W. K. R. MUSGRAVE and I. RITCHIE, *J. Polymer Sci., Polymer Chem.* **13** (1975) 857. Also in "Advances in Polymer Friction and Wear", Vol 5A, edited by L. H. Lee (Plenum Press, New York, 1975) 373.
3. D. T. CLARK and K. C. TRIPATHI, *Nature Phys. Sci.* **241** (1973) 162.
4. D. T. CLARK and H. R. THOMAS, *J. Polymer Sci., Polym. Phys.* (1977) in press.
5. D. T. CLARK, W. SALANECK and A. PATON, *J. Appl. Phys.* **47** (1976) 144.
6. J. M. TEDDER and A. NECHVATAL, "Basic Organic Chemistry", Vol. 2, (J. Wiley, London, 1967).
7. D. T. CLARK and H. R. THOMAS, *J. Polymer Sci., Polymer Chem.* **14** (1976) 1671.

Received and Accepted 20 April 1977.

D. T. CLARK,  
A. DILKS,  
D. SHUTTLEWORTH  
Department of Chemistry,  
University of Durham,  
South Road,  
Durham, UK

## Reply to "Comments on 'X-ray photoelectron spectroscopy studies of polymer surfaces Part 2'"

In implying that the object of our paper [1] was to re-examine the work of Clark, Feast, Musgrave and Ritchie [2] (CFMR), Clark and co-workers [3] have failed to understand our aims. In the introduction to our paper we state: "In the present paper, another pre-treatment is re-examined using X-ray photoelectron spectroscopy (XPS or ESCA). The treatment discovered by Schonhorn and Ryan [4] involves melting polyethylene on to aluminium...". The work of CFMR is only

relevant to our work in one aspect (discussed in detail below).

The statement that our work [1] essentially duplicates that published by CFMR several years ago is inaccurate for the following reasons:

(1) The conditions used by CFMR were very different from those used by Schonhorn and Ryan [4], whose conditions we rigorously followed, both with respect to pressing conditions and the removal of the aluminium film (this latter point is discussed fully below). In particular the temperature used by CFMR was 200°C whereas we used temperatures of 150 and 175°C. CFMR do not quote the time of pressing, this is obviously a vital

variable in any *quantitative* study of the oxidation of polyethylene. Moreover, Clark, Dilks and Shuttleworth [3] (CDS) admit to this variability in comparing the new data\* included in their comment with previous data (in CFMR).

(2) CFMR used an experimental polymer which does not appear to have been characterized, e.g. in terms of melt flow index. We used two well characterized (commercial) polyethylenes, one of our objectives was to study differences in oxidation between low- and high-density polyethylenes under the same conditions.

(3) Perhaps the most important difference is one of objective. CFMR were basically attempting to characterize the level of surface oxidation of polyethylene films to be used in fluorination experiments; they give no adhesion measurements, nor do they discuss polyethylene oxidation in terms of adhesion theories. The introduction to our paper [1] makes it quite clear that our objective was a better understanding of surface treatments and an assessment of current adhesion theories. To this end we were able to compare oxidation levels of polyethylene after melting against aluminium with levels obtained by us for other treatments [5]. Because we followed the procedure of Schonhorn and Ryan [4] the aluminium was removed from the polyethylene film by dissolution, whereas CFMR peeled off the aluminium. In one case we used both methods to compare results; this constitutes the only aspect of overlap with their work. In our paper we briefly concluded that an assumption used by CFMR was incorrect, namely that "On making the reasonable assumption that because of temperature gradients, diffusional phenomena, and the relatively low concentration of oxygen (the only available oxygen being that entrained in the powdered polyethylene sample), that in the sample prepared by method (d)† oxidation was likely to be limited to the first monolayer . . .". We felt that a detailed comparison of data within our paper would be an unnecessary distraction. The total length of these letters

justifies that view. However, since CDS claim that this conclusion is based on a false comparison of data, we present here the arguments leading to our conclusion. Note the following points from our paper [1]:

(i) Our angular variation data for surfaces produced after dissolution of the aluminium show a homogeneous oxygen distribution within the O1s sampling depth (several monolayers)‡

(ii) Our study of surfaces produced by peeling and dissolution techniques show that film failure during peeling results in an exposed polymer surface exhibiting much lower levels of oxidation than the interfacial layer (i.e. that actually in contact with the aluminium during pressing)

(iii) The relative C1s:Al2p intensities for the aluminium foil surface peeled from the polymer indicate that the "top monolayer" (at least) of the pressed film remains on the aluminium after peeling; CFMR observed a similar effect. We specifically showed the additional carbonaceous material to be highly oxidised compared with the residual hydrocarbon on the aluminium foil.

Now despite the fact that pressing took place under nitrogen§, the peeled polyethylene surfaces analysed by CFMR give O/C ratios many times (>5) higher than we observed for peeled surfaces and similar to our surfaces produced by aluminium dissolution (both for pressing *in air*); both sets of data are directly comparable. These points show conclusively that oxidation of polyethylene, under the conditions used by CFMR, extends over several monolayers. Whether or not the residual oxygen in peeled surfaces is confined to the top monolayer, which seems to concern CDS, is an entirely separate issue. Their confusion results from a lack of appreciation of the difference between polyethylene film surfaces produced by peeling or dissolution techniques (this is also evident in CFMR where contact angle data for their peeled surfaces are directly compared with Schonhorn's data [6] (Al dissolved) in order to assess crystallinities).

CDS state "By contrast (to their samples) the

\*One cannot be more specific about this because of the probable heterogeneous nature of oxidation (e.g. amorphous versus crystalline regions).

†This appears to be from films prepared about three years ago; we question the relevance of this data, as the unstabilized films appear to have been stored without special care.

‡Pressed under nitrogen at ~ 200° C.

§CDS describe the difference between the oxidation levels for pressing in air and nitrogen (at 200° C) as 'extensive' and 'relatively low' respectively. Quantifying their peak intensities (Fig. 2 CFMR) we find the difference to be merely a factor of ~ 1.5 in the O/C ratio (as used in our paper).

peeled samples prepared by Briggs and co-workers obviously exhibit extensive oxidation into the sub-surface and bulk as may be readily appreciated from a comparison of the Cls levels for the aluminium foil subsequent to peeling off the polymer film". The data in our paper and in CFMR show (a) very similar Cls:Al<sub>2p</sub> peak intensity ratios for Al surfaces after peeling (and the controls) but (b) O/C ratios some 5× higher in the CFMR surface (pressed in nitrogen at 200° C) than in our peeled surface (pressed in air at 150° C). The available data clearly reject the above assertion of CDS.

The remaining points raised by CDS will be briefly answered. With regard to removal of aluminium by dissolution, our estimated detection limit is in fact ~0.05 monolayers; it is not clear on what basis CDS make their comparative calculation. The point about contacting polymers is also unclear; in using films pressed between PET as controls it was necessary to show that a (potentially oxidized) layer of polyethylene was not transferred on peeling. Our paper reported the negative result of this experiment. Finally we did not claim that unsaturation may be determined by bromine uptake measurements. We reported preliminary data aimed at estimating relative changes in unsaturation. The comments of CDS largely reiterate our own cautious assessment of the data (we pointed out the values obtained were considerably higher than obtained by infra-red analysis); we chose to exemplify crystallinity and side-chain bromination effects since these could change independently of

unsaturation whereas allylic bromination would not. The relevance of the observation that H-bonded HF can be detected in very small quantities (cf our bromine peak intensities) on highly polar polymethacrylate surfaces is questionable.

In conclusion: Our work cannot be regarded as repeating that of CFMR. Whether our work was worthwhile is best judged by those familiar with the field of surface treatments and adhesion. In the interests of objectivity it is hoped the preceding letter is only read in conjunction with this reply and references [1, 2, 4].

## References

1. D. BRIGGS, D. M. BREWIS and M. B. KONIECZKO, *J. Mater. Sci.* **12** (1977) 429.
2. D. T. CLARK, W. J. FEAST, W. K. R. MUSGRAVE and I. RITCHIE, *J. Polymer Sci. Polymer Chem.* **13** (1975) 857.
3. D. T. CLARK, A. DILKS and D. SHUTTLEWORTH, preceding letter.
4. H. SCHONHORN and F. W. RYAN, *J. Polymer Sci. A-2* **6** (1968) 231.
5. D. BRIGGS, D. M. BREWIS and M. B. KONIECZKO, *J. Mater. Sci.* **11** (1976) 1270.
6. H. SCHONHORN, *Macromolecules* **1** (1968) 145.

Received 27 May  
and accepted 8 June 1977

D. BRIGGS  
*ICI Ltd, Corporate Laboratory,  
Runcorn Cheshire, UK*  
D. M. BREWIS,  
*Leicester Polytechnic,  
Leicester, UK*