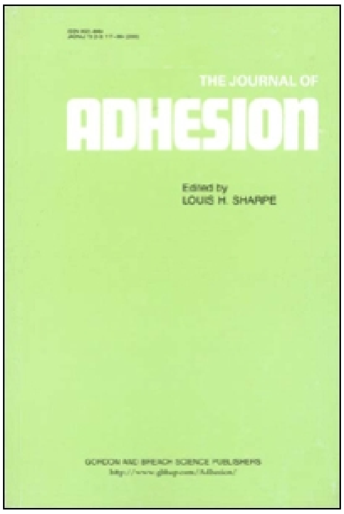

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Sorption of Iodine onto Corona-Modified Polyethylene

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Nitrogen corona treated polyethylene was found to adsorb larger quantities of iodine from dilute solution ($<10^{-4}$ M) than an equivalent untreated polyethylene. The extent of the preferential adsorption is related to the length of treatment in the corona and also upon the initial concentration of the iodine solution. This preferential adsorption is suggested to occur via an electrostatic mechanism through charges induced into the polymer surface by the corona.

INTRODUCTION

It has been well established in many laboratories that subjecting a polymer surface to a corona discharge will greatly enhance surface properties such as wettability and surface energy. These changes have enabled processes such as dyeing, printing and bonding to be achieved more effectively. The exact nature of the changes occurring in the polymer surface from such treatments depends upon the type of gas used in the corona. For oxygen containing gases this has been almost universally accepted as being the direct result of the oxidising action of the corona. However, for inert gas coronas, particularly nitrogen, immediate explanation is difficult. It appears that no detectable change in chemical structure of the polymer surface arises from this treatment[1] nor is there any evidence of crosslinking[2] or degradation. Electron microscopy, both transmission and scanning, does not reveal any change in the topography of the polymer sheet from this treatment as opposed to, e.g., the production of

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"bumps" in the case of air corona treated polyethylene[3]. Yet, exposing polyethylene to a nitrogen corona increases its capability for autohesion more so than an air or oxygen corona[2]. One disadvantage is that the effect decreases rapidly after one day and this decrease is even accelerated under certian storage conditions.

High energy radiation of polymers is known to promote free radical formation which may lead to crosslinking or degradation. In view of this it is feasible that bombardment with the active species associated with the corona discharge may give rise to the formation of perhaps relatively stable free radicals. These free radicals would then be responsible for the higher autohesion of polymers arising from the corona treatment. Free radicals have been detected in polymers after electrical discharge treatment at lower pressures by Bamford and Ward[4] and Kelen and Dick[5].

In order to establish the existence of free radicals, series of measurements were made using Electron Spin Resonance (ESR) techniques. A comprehensive search for free radical formation on nitrogen corona treated polyethylene was made using a Varian Model 4250 ESR spectrometer with a variety of sample forms. However, these experiments failed to produce even a slight indication of the presence of free radicals. Application of the use of free radical scavenging techniques appeared to be more successful. When a corona treated polyethylene sample and an untreated sample were immersed into a solution containing free radioiodine, I^{131}, the treated sample gained about five times more iodine than the untreated sample. Perhaps this increase in iodine uptake arises from reaction with free radicals or unsaturated groups present in the polymer surface. The following work entails an investigation into these possibilities.

EXPERIMENTAL

Materials

A high density polyethylene film of thickness 0.002 inches, obtained from Union Carbide Co., was used throughout. The samples were cleaned by immersing them in a detergent solution at 60°C for a few minutes, rinsing with water followed by methanol and then drying in vacuo for 48 hours.

The apparatus and gas used for the corona discharge treatment of this film have been described elsewhere[1].

Iodine Radioiodine, I^{131}, separated isotope was received as an aqueous solution of sodium iodide in sodium sulphate[6]. This iodide solution was added to a measured quantity of crystalline sodium iodide contained in a volumetric flask and a few drops of water were added to dissolve this. The iodine was liberated from solution by adding slightly in excess of the required stoichiometric quantities of hydrogen peroxide and sulphuric acid. The whole was then diluted to known volume. The iodine was extracted from aliquots of the aqueous phase into a carbon tetrachloride phase and diluted further. For the sorption measurements a solution was divided into the number of aliquots required for testing.

Iodine sorption measurements

Samples of polyethylene film, 2.5 cm. diameter circles, were immersed and agitated manually in the iodine solution for a known time. These were then rinsed, dried and mounted ready for counting. Rinsing was accomplished, in the case of carbon tetrachloride solutions, with ether. The samples were mounted centrally on cardboard planchets, 2.0 inches diameter, and covered with a thin polyethylene terephthalate (Mylar) film held down with adhesive tape. Counting was carried out on a Beckman Wide Beta II planchet counting system[7]. All counts were normalized to a standard time using the decay law:

$$N = N_0 \exp(-\lambda t)$$

where N = Number of counts at time t.
N_0 = Number of counts at time $t = 0$.
λ = 0.693/Half life of iodine 131 (in units of t)

It was adequately shown that no change in the normalised iodine content of the samples occurred after several days, and also inversion of the samples on the planchet did not affect the count rate. In measuring the specific activity of the iodine solutions, a small aliquot, 1 μ litre, was spotted on to a glass filter pad followed immediately by a few drops of sodium hydroxide solution, thus preventing loss of iodine by evaporation.

RESULTS

The primary objective was to establish whether or not iodine is held to a nitrogen corona treated polyethylene film by reaction or adsorption. To ascertain this samples of the corona treated polyethylene (15 min. at 15 KV in nitrogen) have been immersed in carbon tetrachloride solutions containing 10^{-5} M Iodine for varying lengths of time. These samples were analysed for iodine uptake and then washed for 24 hours in flowing water. The amount of iodine remaining on the film was then determined. Similar experiments of iodine sorption were carried out with untreated polyethylene. Figure 1 gives the results of these experiments. It appears that there is no initial rapid uptake of iodine by the treated samples indicative of a fast chemical reaction

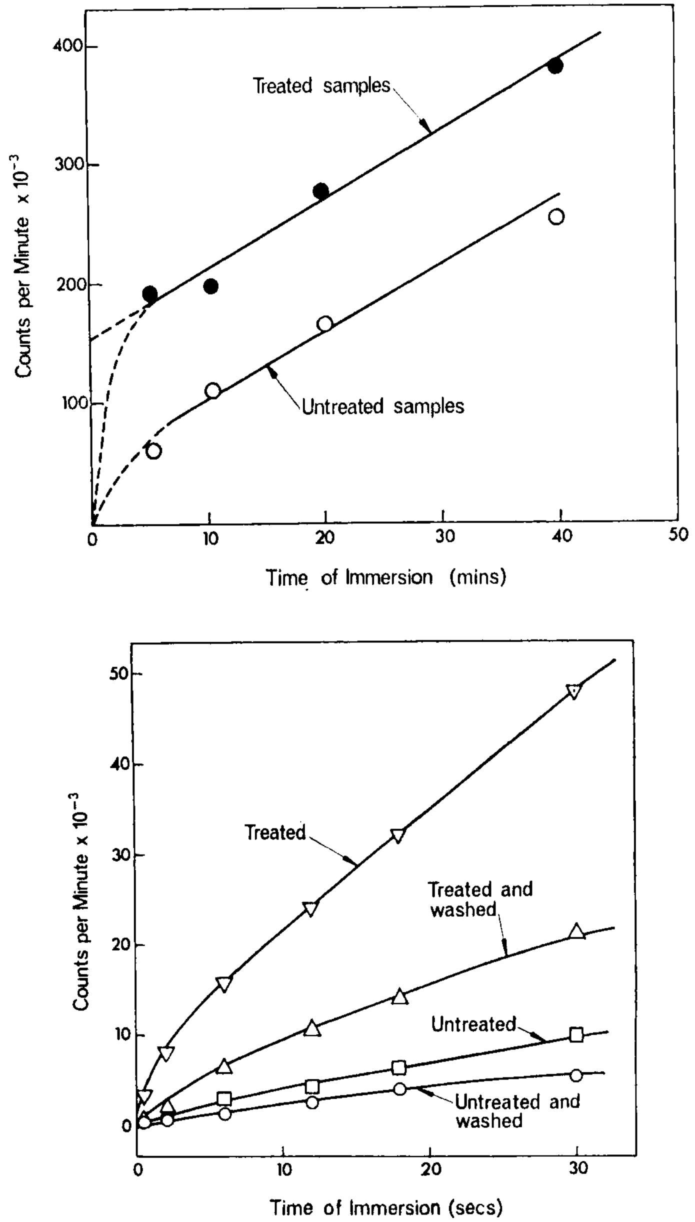

FIGURE 1 (a) Variation of iodine uptake by polyethylene treated in a nitrogen corona (15 min. 15 KV) with different times of immersion in a 10^{-5} M I_2 in carbon tetrachloride solution; (b) Same but for short immersion time. The time of washing in both cases was 48 hours in flowing water.

expected if free radicals were present. Rather there is a gradual increase in iodine uptake with the curves in Figure 1 having the appearance typical of absorption isotherms. Furthermore, on prolonged washing much of the iodine is removed. The possibility of a slow reaction with unsaturated or oxidised groups within the polymer surface is doubtful. Previous infra-red spectroscopy measurements[1] did not reveal any change in C=O and C=C groupings on the surface of polyethylene induced by a nitrogen corona. It may be that the nitrogen corona treatment is able to render any reactive groups that may be present more accessible to reaction.

These explanations become even more doubtful when the concentration dependence of the iodine solution on the iodine uptake is examined. Figure 2 illustrates the variation of the ratio of iodine taken up by a nitrogen corona treated sample over that of an untreated sample of polyethylene when these are immersed into iodine solutions of different concentrations. The samples were washed prior to the analysis by counting. It was apparent that for high iodine concentrations no difference in iodine uptake prevailed, whereas at concentrations below 10^{-4} M iodine the preferential uptake of a treated

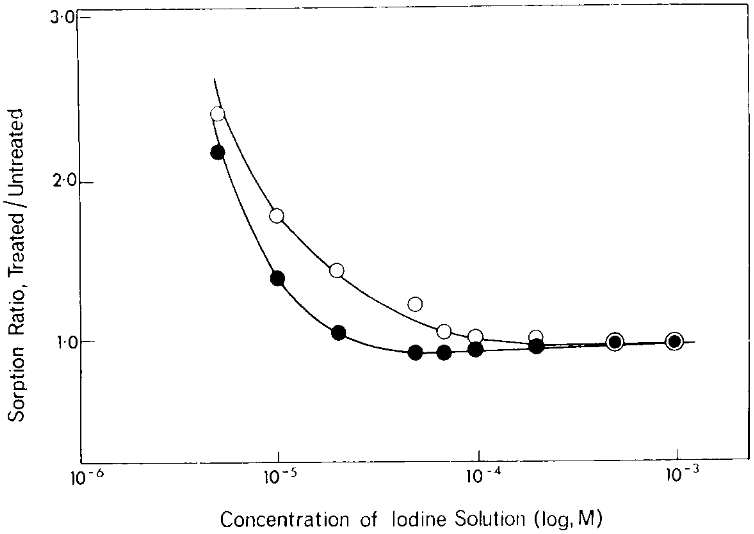

FIGURE 2 An illustration of the difference in iodine uptake by a corona treated polyethylene film to an untreated film when immersed in iodine solutions of various concentrations.

○ 1 hr. corona treatment
● 15 min. corona treatment

sample commenced to increase very rapidly with decrease in iodine concentration. For a solution containing solely carrier-free radioiodine, $\sim 10^{-9}$ M I^{131}, this ratio was particularly high.

The uptake of iodine has been measured as a function of time of treatment of the polyethylene in a nitrogen corona (15 KV). The polyethylene samples were immersed for ten minutes in 50 ml. aliquots of 10^{-5} M iodine in carbon tetrachloride solution. Interpretation is in terms of the excess amount of iodine taken up by a treated sample over that of an untreated sample. The iodine uptake of polyethylene does increase markedly for high treatment times in a nitrogen corona as shown by the curve in Figure 3. Similar results to those obtained for nitrogen corona treated polyethylene have been observed when an argon corona (3 KV) was used.

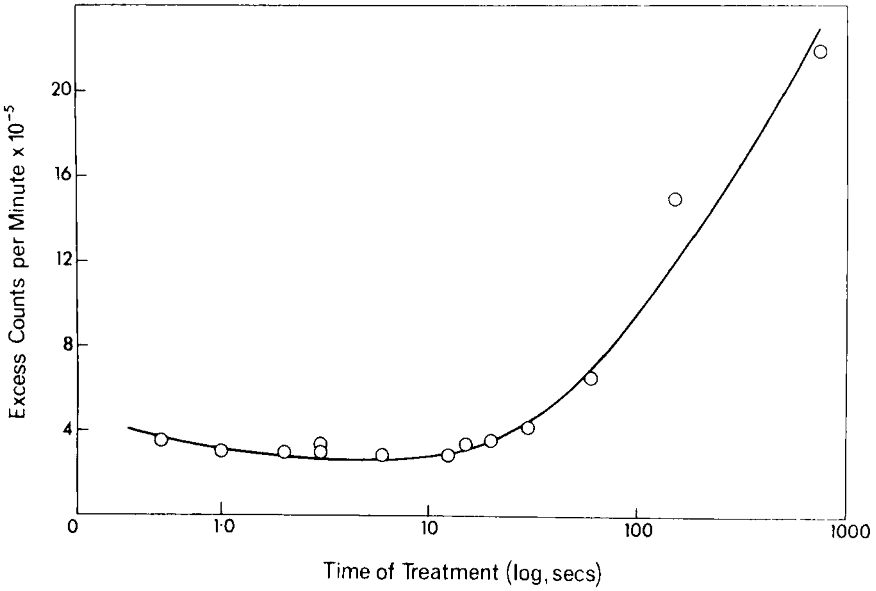

FIGURE 3 Variation of iodine sorption of polyethylene after different times of treatment in a nitrogen corona (15 min. 15 KV).

DISCUSSION

In explaining these results it is reasonable to assume that the iodine is being adsorbed by the polymer surface. Very little information is available concerning the sorption by polymers of anions or neutral molecules, in trace quantities, from solution. Beneš and coworkers[8,9] have made a series of investigations on the sorption of cationic elements on to polymers. They conclude that sorption in these cases may proceed via a physical mechanism and/or chemisorption. There is every indication that these mechanisms also obtain for anionic elements. Other mechanisms may prevail[8] and much will depend, of course, on the species present in solution and the state of the polymer surface. Elements that are easily hydrolysed may be sorbed mostly in an electrostatic manner or by ion exchange in an electric double layer on the polymer surface.

As far as the state of trace quantities of iodine, 10^{-7} M to 10^{-5} M, in solution is concerned, little is known but it does differ markedly from its state in more concentrated solutions[10]. In forming the iodine solutions it was necessary to oxidise the iodide in an aqueous acidic solution of hydrogen peroxide. It is in this environment, at low concentrations, that the produced molecular iodine changes state. This was evident from the slow disappearance of the yellow iodine colouration without loss in activity, i.e. total iodine concentration. Kahn and Wahl[11] have oxidised iodide ion, $\sim 10^{-7}$ M, with sulphuric acid solutions of cerium (IV) or dichromate ion. They have found three uncharacterized species not readily exchangeable with I^-, I_2 or IO_3^-

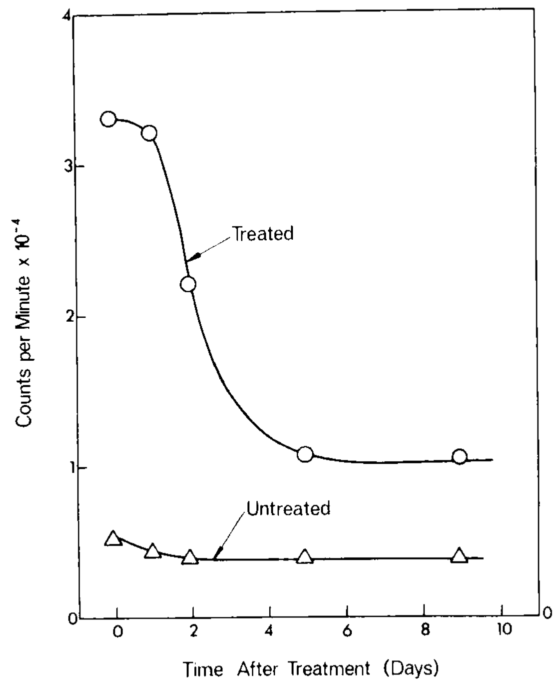

FIGURE 4 Decrease in the uptake of iodine for samples treated in a nitrogen corona (15 min. 15 KV) and stored for different times before carrying out sorption measurements.

together with these species. Once these uncharacterized species have been produced they are not easily oxidised or reduced. They are more easily adsorbed than I^- and I_2[12]. There is a concentration dependence on the production of some of these species which, Eiland and Kahn[12] have shown, increases with decrease in iodine concentration. The increase is slow at first for concentrations of 10^{-3} to 10^{-5} M iodide, but increases rapidly for concentrations below 10^{-5} M iodide. This correlates well with the previous mentioned findings in Figure 2 of a concentration dependence of the sorption from iodine solutions.

It is not unreasonable to suppose that the solutions used in this work contain charged iodine species other than the free iodine. Should this be correct then a possible explanation for the increased sorption of iodine by a corona treated polyethylene sample could be via an electrostatic attraction by unlike charges present in the polymer surface. It should be mentioned that the polyethylene samples carry a very high static charge after the corona discharge treatment. In the absence of any chemical or physical change in the polymer surface arising from the nitrogen corona, these explanations based on an acquired surface charge would appear to be most reasonable.

A further correlation between the iodine sorption and the nature of the corona treated surface has been observed. When nitrogen corona treated polyethylene samples are stored they lose both their static charge and their ability to give increased autohesion[2]. In conjunction with this the iodine sorption of similarly treated samples has been found to decrease rapidly after two days storage, see Figure 4.

CONCLUSIONS

These results suggest that free radicals are not formed in polyethylene by a nitrogen corona discharge. The nitrogen corona treatment is instrumental in enabling polyethylene to adsorb more iodine from dilute solution than when not treated. This increased surface activity is suggested to result from a corona induced surface charge. The results may also give a further insight into the behaviour of iodine at trace concentrations, where it is believed that under certain conditions the iodine dissociates into mainly charged species.

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