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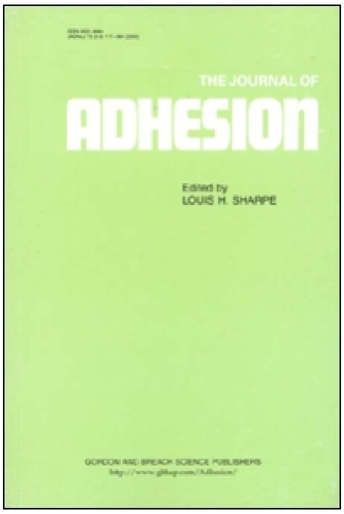

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Nitrogen Corona Activation of Polyethylene

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To cite this Article Evans, J. M.(1973) 'Nitrogen Corona Activation of Polyethylene', The Journal of Adhesion, 5: 1, 1 — 7
To link to this Article: DOI: 10.1080/00218467308078433
URL: http://dx.doi.org/10.1080/00218467308078433

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J. Adhesion, 1973, Vol. 5, pp. 1–7

Printed in Northern Ireland

Nitrogen Corona Activation of Polyethylene

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(*Received February* 23, 1972)

Experiment has shown that the nitrogen corona-induced autohesion of polyethylene and the nitrogen-corona induced sorption of iodine by polyethylene both follow similar mechanisms. The controlling factor is postulated to be the formation of short-lived electrets within the polymer surface.

INTRODUCTION

A series of experiments has been initiated in this laboratory to investigate the use of the corona discharge as a means of activating a polymer surface for enhanced adhesive properties. Arising from this work[1] was the problem of establishing the reason for the increase in autohesion of polymers, particularly polyethylene and polypropylene, after treatment with a nitrogen corona discharge. It appears that no detectable change in the chemical structure of the surface arises from this treatment. Distinction may be made where nitrogen containing traces of oxygen produces marked changes in the infrared spectra due to the presence of oxygen containing groups[2]. Other experiments have indicated the absence of degradation, crosslinking[1], free radical formation[3] and alteration of the topography of the polymer surface[4]. However, from iodine sorption measurements[3] it appears that the increase in surface activity may be due to charge effects induced by the corona.

A corona discharge gives rise to a highly complex environment in which

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changes in all forms of physical behaviour occur, e.g. electricity, light, heat and sound. The corona itself is composed of ions, atoms and other activated species which impinge upon the sample. This invariably produces high localized surface temperatures which together with the strong electrical field could produce conditions beneficial to electret formation. Here the term *electret* is being used to cover events occurring in the surface region, such as trapped ions and electrons or dipole orientation, for example. Consequently it is advantageous to investigate the proposal that the corona discharge produced between two parallel plates using an AC source, as opposed to the commonly used DC source, is capable of inducing electret formation in a polymer surface. Support for this hypothesis may be had from the work of Zichy[5] who made a study of the effects of a DC corona discharge on polypropylene film. He maintains that by using discharge potentials below those required for the inducement of a corona, electrostatic charges produced in the polymer surface were of the type associated with electret formation.

The foregoing work attempts to pinpoint the exact nature of the contributing factor in the polymer surface activation by a nitrogen gas corona.

EXPERIMENTAL

All polymer samples, nitrogen gas and apparatus used were as previously described[2]. Polyethylene (B) was used in the autohesion measurements.

Autohesion Test: For this test coupons, 0.5 × 1.5 cm, were cut from the sample and an overlap join, 0.25 sq. cm., formed with the treated surfaces together. Adhesion was effected by pressing at 5.7 Kg/sq. cm. and 45°C for two minutes. The specimens were allowed to cool before measurement of the bond strength using a motorised Chatillon Spring Tester described elsewhere[6]. An average of twleve determinations was taken for each treated sample.

RESULTS AND DISCUSSION

When a polymer has been subjected to a corona discharge it acquires a fairly high overall static charge on the surface. The superficial charge is predominantly a homocharge and treated surfaces will repel each other. Two methods were invoked as a means of detecting the presence of the surface charge. One was the use of an electroscope and the other the formation of Lichtenberg figures[7]. The latter were produced by sprinkling the surface with powdered (# 90) Jeweller's rouge and shaking off unretained powder. An example has been given elsewhere[1]. Removal of the superficial charge may readily be achieved by any conventional method. However, different removal methods have different effects on the subsequent surface properties. The use of light brushing with an antistatic brush containing a radioactive palladium source does not appear to change the wettability or autohesion of corona treated polyethylene. This is in contrast to exposure to vacuum which has a marked effect for short treatment times, and immersion into liquids which gives even more pronounced effects. The latter procedure has been employed to investigate the effects of removing the corona induced surface charge on the subsequent adhesive properties of polyethylene.

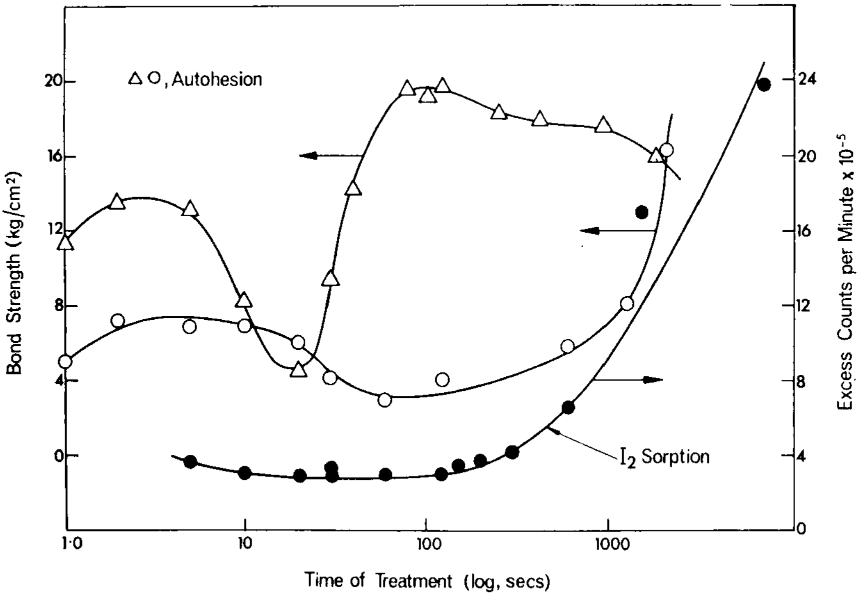

FIGURE 1 Variation of the autohesion of polyethylene with length of treatment in a nitrogen corona, both before and after water immersion prior to bonding. Also included is the variation of iodine sorption of polyethylene with time of treatment in a nitrogen corona.

Autohesion measurements were made on polyethylene after subjecting it to a nitrogen corona (15 KV) and also when the treated samples had been immersed in water and dried prior to bonding. The effect of this treatment is illustrated in Figure 1. The water immersion was found to be an efficient charge removal agent and it was only at very long treatment times that sufficient residual activity remained to give increased bonding. Also included in Figure 1 is the variation of iodine sorption with time of nitrogen corona treatment for polyethylene, taken from the previous article[3]. It is apparent that the autohesion of polyethylene follows the iodine sorption more closely after the water immersion. It has already been suggested that the iodine sorption process may be related to induced charges in the polymer surface. Since both water immersion or immersion into the iodine solution removed the superficial charge, any residual charges, if they exist, must predominate within the polymer surface matrix.

Evacuation has also been shown to remove the surface charge from corona treated samples, but not to lower the autohesive capacity to the extent of a water immersion. Indeed, no difference in bonding after evacuation was detected for polyethylene samples treated for times longer than 100 seconds. The effect was to displace the autohesion curve in Figure 1 slightly to the right. Lichtenberg figures also failed to form on polyethylene treated in a nitrogen corona for varying times and then exposed to a vacuum of $<10^{-3}$ torr for thirty minutes.

Explanation of these results may be afforded in light of the proposed electret formation as follows. In the widely accepted two charge theory of electrets[8], there exists a deep seated charge within the polymer matrix and a corresponding superficial surface charge. Examination of the superficial charge distribution may give some indication of the electret charge distribution. A more precise indication of the charge distribution within the polymer surface is available from the variation of the concentration of iodine sorbed on to the treated polymer, as this was suggested to occur via occluded charge effects. Radiographs of such a polyethylene surface do in fact have a mottled appearance as shown in Figure 2. Lichtenberg figures of the treated polyethylene surface before charge removal also have a similar mottled appearance, see Figure 8 in reference[1]. This type of electret would be that expected from an AC discharge where a distribution of positively and negatively charged areas would pertain.

Methods used to remove the surface charge differ in their action. Evacuation is known to remove surface electret charge by a process of ion desorption[9]. After this process a conventional volume polarised electret will gradually reproduce the surface charge. This was not practicable in this case as the time constant for this action is greater than the decay rate of the observed effect. Evacuation would not be all that efficient in removing melt trapped charges formed at the high localized temperatures attained in the corona discharge. Charge removal by liquid immersion is more efficient as its action is to short adjacent charges. This only becomes ineffectual at the long treatment times when presumably deeper inaccessible charges prevail.

It has also been shown that for the same times of treatment of polyethylene in a nitrogen corona at different temperatures, there is an increase in autohesion with increase of treatment temperature. An increase in autohesion also holds with increase in bonding temperature for polyethylene samples treated for the same length of time at the same temperature in a nitrogen corona[1]. This is in accord with the basic processes of the production and release of induced

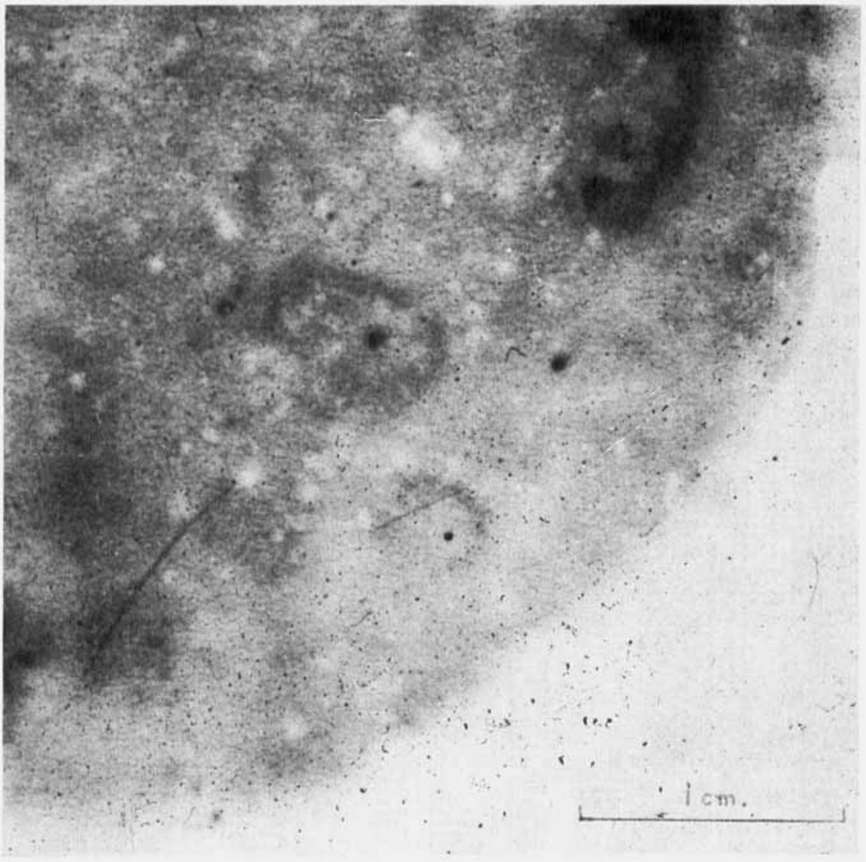

FIGURE 2 Autoradiograph of iodine I^{131}, sorbed on to corona treated (0.25 sec) polyethylene film. The light patch on the right hand side corresponds to the position of one of the glass spacers used during the corona discharge treatment.

charges. The possible measurement of depolarisation currents liberated from the treated samples may produce further correlations and may even give an insight into the localized surface temperatures produced in the corona[10].

The decay in autohesion[1] and iodine sorption[3] with storage after treatment, collated in Figure 3, together with a corresponding lack of Lichtenberg figure formation indicates the semipermanent nature of the electrets. The correlation in Figure 3 suggests that similar mechanisms exist for the iodine sorption and autohesion of polyethylene.

A further result of the variation in charge distribution is prevalent in the autohesion tests. For these tests an average was taken of twelve separate

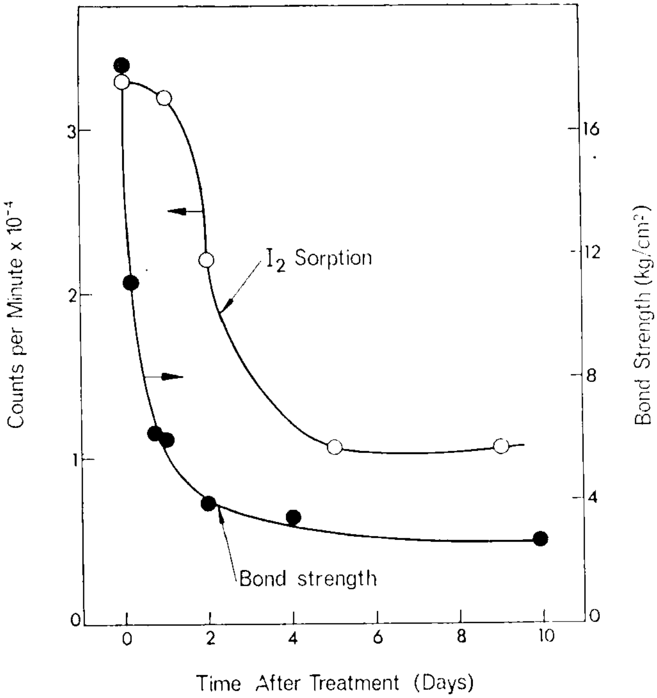

FIGURE 3 Decay of bonding ability and iodine sorption capacity of polyethylene with time after treatment in a nitrogen corona (15 min, 15 KV).

measurements made on coupons cut from the same treated sample. In most cases there was an upper limit for the bond strength where two or three values were obtained, the majority lay about the average and in some cases one or two fell much lower. The best bonding would be obtained by the ideal cohesion of thermally liberated surface molecules perhaps via an electrostatic mechanism, e.g. dipole-dipole interaction. For the very low bonding values, much may relate to the initial state of the polymer surface even though samples were carefully selected for optimum smoothness. It should be mentioned that bond strengths greater than 22 kg/cm^2 were not attainable. This arose through the test coupons exceeding their elastic modulus and necking was induced in one coupon until the bond finally ruptured.

Comparison of the bond strength curves after air, oxygen[1], and nitrogen corona treatment found them superimposable for treatments up to 1 second. Similar mechanisms presumably pertain at these low treatment levels. The occurrence of a minimum at around 10–20 seconds in the bond strength versus time of treatment curves appears to be a real effect for most coronas and remains as yet unexplainable. It may be related to some kind of interplay between the crystalline and amorphous regions in the polymer surface which may have different levels of resistance to corona activation.

CONCLUSIONS

It is suggested that the principal result of a nitrogen corona discharge treatment of polymers is the formation of short lived electrets within the polymer surface. These electrets would be the controlling factor in improving the wettability and autohesion of polyethylene. Depending upon the time and temperature of subjection to the nitrogen corona, electrets would exist at various depths and concentration in the polymer surface. This highly active surface obtained for inert gas coronas could be useful for many after treatments where complications in chemistry would arise from coronas where oxidation or other chemical modification occurs. Furthermore, most physical and chemical properties, mechanical properties and topography are not changed by inert gas coronas.

Whilst this work has been confined to polyethylene it should be mentioned that similar effects have been observed with other polymers notably polytetrafluorethylene, polyvinyl chloride, polyvinylidene chloride, polypropylene and polystyrene.

Acknowledgements

The author appreciates the many helpful and stimulating discussions with Drs. D. A. I. Goring and C.-Y. Kim, throughout the whole of this work.

This work was supported by the Pulp and Paper Research Institute of Canada.

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