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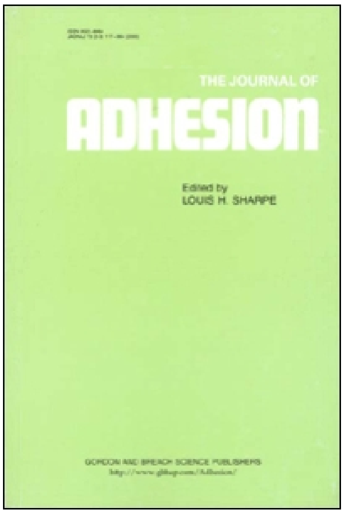

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The Influence of Oxygen on the Nitrogen Corona Treatment of Polyolefins

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The Influence of Oxygen on the Nitrogen Corona Treatment of Polyolefins

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The resultant surface activation of polymers by corona discharges has been found to be markedly influenced by the type and purity of gases used in the corona. In this work it is shown that for the nitrogen gas corona treatment (15 KV, 15 mins) of polyethylene and polypropylene, traces of oxygen, $>0.5\%$ and $<0.15\%$ respectively, are sufficient to produce chemical changes in the polymer surface.

INTRODUCTION

One of the standard ways of improving the wettability of polymers, particularly polyolefins, is to subject them to a corona discharge. This will produce a surface which may be more easily dyed, printed and bonded. Relatively few studies have been made to elucidate the chemical nature of changes produced on a polymer surface from this treatment especially when inert gases are used in the corona. An understanding of any chemical changes may give an insight into the processes involved in producing the highly active surface.

It has been shown[1] that oxygen, nitrogen and air coronas are all instrumental in improving the wettability and surface energy of polymers. Preliminary infra-red spectroscopy measurements in this laboratory[2] have indicated that both air and oxygen corona treatments give changes in the chemistry of

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the treated polymer surface whereas pure nitrogen corona does not give any apparent change. Similar findings have been reported by Koikov *et al.*[3] for polyethylene, polystyrene and polyethylene terephthalate. Stannett and Meats[4] also found no apparent change in the nitrogen corona treatment of polyethylene even under extreme conditions. However these results are contrary to those of Kelen and Dick[5] who found a much increased unsaturation in polyethylene after a nitrogen corona. Carlsson and Wiles[6] have also reported changes in the infra-red spectrum of polypropylene after exposure to a nitrogen corona.

Arising from this controversy and from incidental experiments conducted in this laboratory it is likely that the purity of the gases used in a corona greatly influences the type of surface produced. This observation is consistent with that of Ieda *et al.*[7] who have been investigating the decay processes of surface charges produced on polyethylene films from corona treatment with different mixtures of nitrogen and oxygen gases. They found that trace quantities of water and carbon dioxide present in the corona restricted any meaningful interpretation of the resultant data.

This article is concerned with whether trace quantities of oxygen containing gases, particularly oxygen itself, do in fact influence the nitrogen corona treatment of polymers. Polyolefins have been chosen to simplify the chemistry of the processes. The experimental conditions necessary for subsequent investigations into the inert gas corona treatment of polymers have been established.

EXPERIMENTAL

Materials

Polyethylene A—A high density polyethylene film of thickness 0.002 inches obtained from Union Carbide Co.

Polyethylene B—A low density polyethylene sheet 1/32 inch thick (C.I.L. 220 G) obtained from Dow Chemical Co.

Polypropylene—Film of isotactic polymer 0.003 inches thick obtained from Hercules Chemical Co.

All samples were cleaned by immersing then 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.

Oxygen gas was obtained as 99.6% purity from Liquid Air, Canada, and used without further purification excepting that it was passed through a one inch diameter by four foot long silica gel column prior to admitting it to the test apparatus.

Nitrogen gas, obtained as 99.997% purity from Matheson Co., Whitby, Ontario, was further purified by passing through two glass columns, 3 ft. × $\frac{3}{4}$ inches diameter, containing pure copper turnings heated to 475°C. Analysis of the gas treated in this manner by mass spectrometry showed it to be free of oxygen.

Apparatus

A diagrammatic representation of the system used for treating the polymer samples is given in Figure 1. The cell, see insert, consists of two stainless steel electrodes $2\frac{1}{2}$ inches in diameter each covered with a 0.03 inch thick glass plate as a dielectric. The sample is placed on the lower electrode and the top electrode is supported directly over this with 0.12 inch thick glass spacers. The treated area of the sample is thus a $2\frac{1}{2}$ inch circle. The top electrode is connected to the output of an A-C power supply (60 Hz, 15 KV) and the lower electrode to ground.

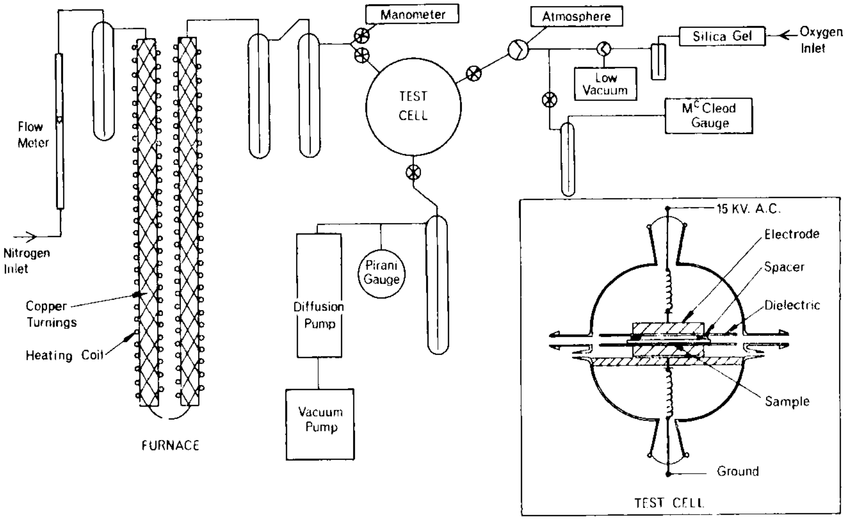

FIGURE 1 Diagram of apparatus used for the nitrogen corona treatment of polymers with modifications for oxygen gas treatments.

In operation, the cell with the sample in place, was evacuated to $<10^{-4}$ Torr for about 30 minutes and then isolated from the high vacuum source. Nitrogen gas was then admitted into the cell to atmospheric pressure and the cell was again evacuated. The cell was again filled with nitrogen and then opened to atmosphere via a small bleed, maintaining the nitrogen flow rate at 25 ml/min.

In cases where mixtures of oxygen and nitrogen gases were required a stationary gas phase was used. The procedure for filling the cell was slightly different. Following evacuation of the cell it was found expedient to allow oxygen to enter the cell to a certain pressure and thence to fill the cell to atmospheric pressure with nitrogen gas. In any event the nitrogen was introduced slowly at slightly above atmospheric pressure to prevent any of the mixture recirculating into the nitrogen supply. Furthermore, the experiments were conducted in the order pure nitrogen first and gradually increasing the oxygen content to pure oxygen to aid achievement of accurate mixtures.

Infra-Red measurements

A Wilks Model 9 Multiple Internal Reflection (MIR) attachment was used in conjunction with a Unicam SP 200G infra-red spectrophotometer. Further spectra were also obtained by modifying the MIR attachment to fit into the cell-well of a Unicam SP 100G infra-red spectrophotometer.

Measurements were made on rectangular samples (1.7 × 0.8 cm) cut from the treated areas of the films and held on each side of a KRS 5 crystal with slightly smaller pieces of thin latex rubber sheet as compression agents. The angle of incidence used was 45° and the scanning speed was set slow.

Direct transmission spectra of the bulk films were obtained using either or both the Unicam SP 100G and SP 200G infra-red spectrophotometers.

RESULTS AND DISCUSSION

It has been well established that exposing a sample of polyethylene to a nitrogen, oxygen or air corona for a duration of fifteen minutes at 15 KV A-C will increase autohesion by a factor of at least six times that obtained with untreated material. The method used in deriving this comparison has been given elsewhere[8]. All the samples used were given this same time of corona treatment chosen to achieve a suitably advanced stage of surface activation.

Examination of the MIR infra-red spectrum of the untreated polyethylene (A) surface reveals several differences to that of the corresponding bulk adsorption spectrum. It was found that the surface contained a fairly broad peak with predominant adsorption at frequencies of ~1655 and ~1750 cm^{-1}. These peaks presumably arise from C=C and C=O groupings which occur on the film during manufacture or from subsequent surface oxidation.

On subjecting polyethylene sample (A) to a pure nitrogen corona, no difference in the MIR spectra to that of the untreated sample was detectable. Similar effects were found when nitrogen containing 0.08%, 0.10%, 0.2% and 0.5% of oxygen gas was used in the corona treatment. When a gaseous mixture of 0.8% oxygen in nitrogen was used a change in the MIR spectra

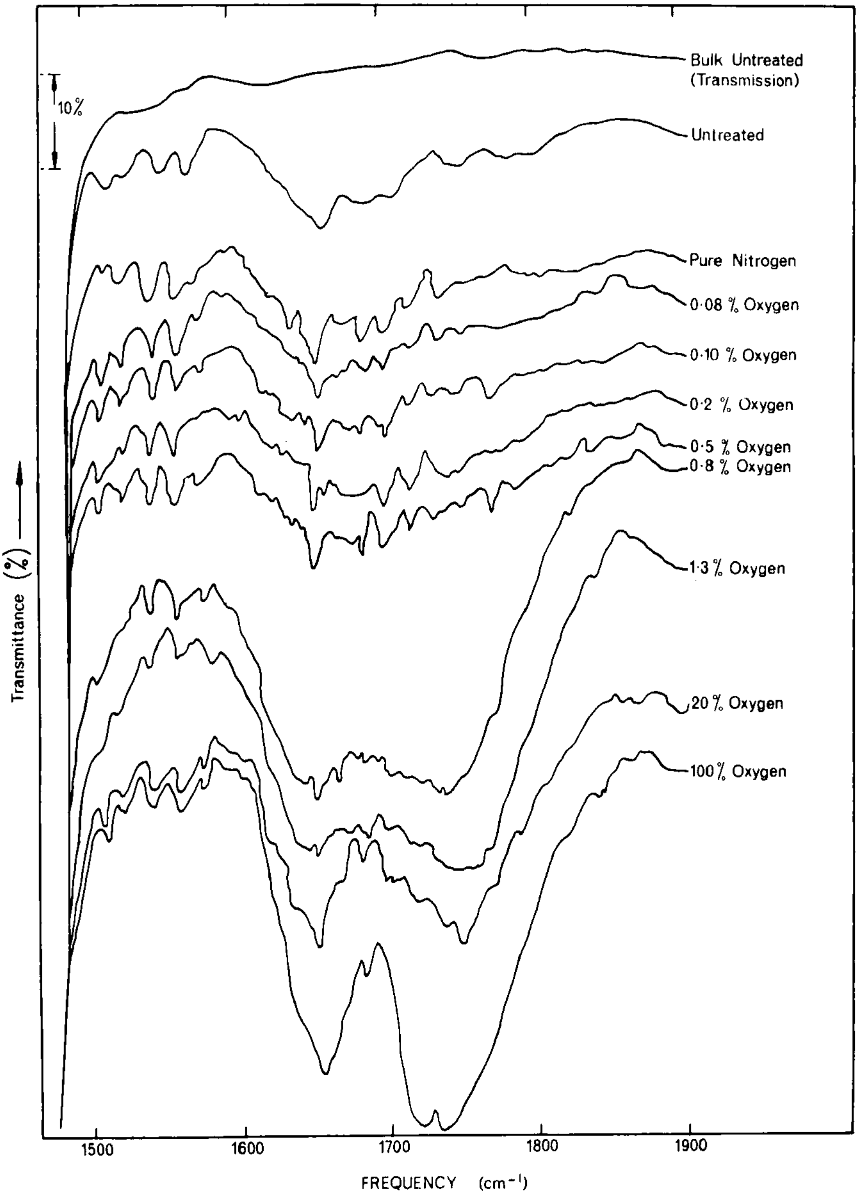

FIGURE 2 MIR infrared spectra of polyethylene surfaces, measured on a Unicam SP100G, after treating in nitrogen/oxygen corona discharges. Also included are the bulk and surface spectra of the untreated polyethylene.

was observed. This is shown in Figure 2 where a marked change occurs between the spectra obtained for treatments using nitrogen gas containing 0.5% and 0.8% of oxygen. Adsorption peaks at 1755 and 1655 cm^{-1} frequencies are prominent for the cases of 100%, 20%, 1.3% and 0.8% oxygen in nitrogen mixtures. Although not illustrated here, further peaks appear at ~865 and 1295 cm^{-1} for nitrogen gas containing 20% and 100% of oxygen. These changes in the MIR spectra describe the progress of the oxidative degradation occurring during the corona treatment of which detailed discussions have been given elsewhere[6,9,10]. Sharples[9] also cites cases where carboxyl, nitrate, nitrite, ether linkages and ozonides have been identified, presumably from corona discharge treatments in air. A quantitative interpretation of the spectra was not attempted at this stage but will be reported subsequently.

Noticeable also was the clarity and definition of the spectra derived from pure nitrogen and pure oxygen corona treated polyethylene. The peak broadening associated with the spectra from the gaseous mixtures would arise from the complex reactions occurring in such coronas. In no instance did the treatment with the pure nitrogen corona give any increase in the unsaturation of the polyethylene surface as has been reported by other workers[5,6].

For polypropylene samples very similar effects were found. There was no change in MIR spectra for nitrogen corona treated samples whereas for coronas of nitrogen containing only 0.015% oxygen a marked change occurred at a frequency of ~1655 cm^{-1}. Practical difficulties prevented attaining lower proportions of oxygen in nitrogen. Figure 3 shows the change produced in the MIR spectra of a polypropylene surface by corona discharge treatments in various mixtures of oxygen and nitrogen. The relative ease of degradation of polypropylene to polyethylene would be related to the more numerous pendant methyl groups of the polypropylene chain.

Another surface analysis technique, reported by Johnson[11] was initially applied to polyethylene (B) samples. In this technique the surface of five samples, a surface area of 24.5 sq. in., was lightly abraded with potassium bromide powder. The powder was then pressed into a disc ensuring that the contaminated potassium bromide was mainly distributed in the central portion. The disc was analysed by direct transmission infra-red spectroscopy using both the Unicam SP 100G and SP 200G spectrophotometers. No change in the absorption spectra of the surface of polyethylene was detected after subjecting it to nitrogen corona discharges at 15 KV for 15 minutes or 1 hour.

The complete absence of any form of chemical change in the polyolefin surface through subjection to a nitrogen corona was not altogether unexpected, as an examination of the surface by scanning electron microscopy and transmission electron microscopy had revealed no topographical change

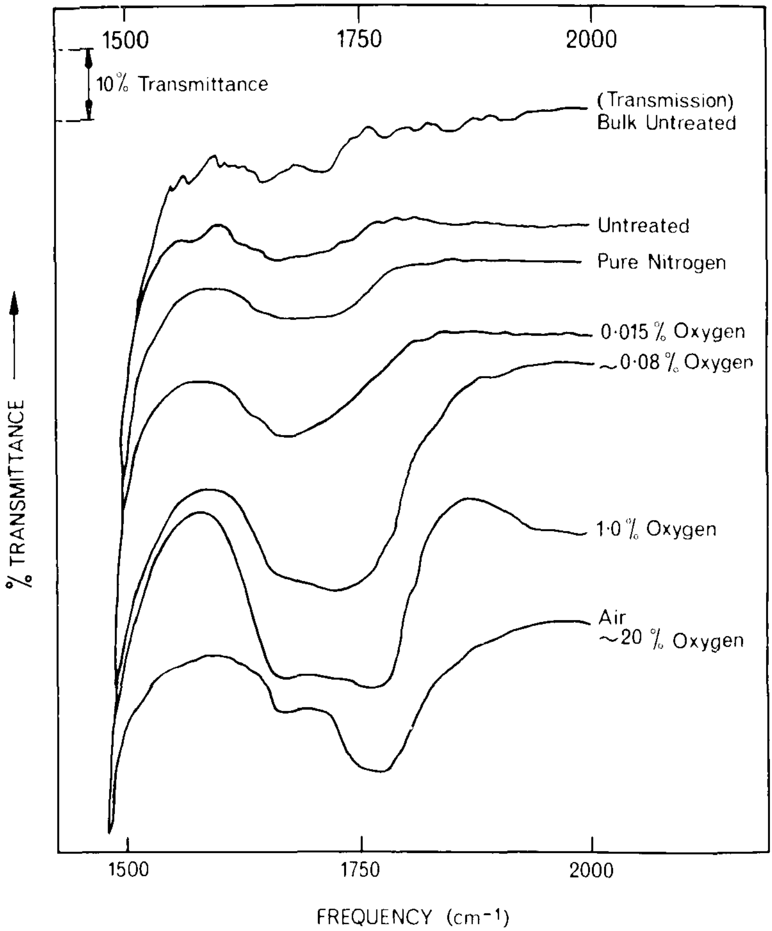

FIGURE 3 Comparison of MIR infrared spectra obtained for polypropylene after corona discharge treatment in mixtures of nitrogen and oxygen, using a Unicam SP 200G spectrophotometer.

from this treatment. In contrast a decidely rough surface was produced when polyethylene was exposed to oxygen or air corona discharges[12].

CONCLUSIONS

These results do indicate that it is possible to obtain a high level of polymer surface activation without unnecessary surface oxidation using pure nitrogen corona discharges. The purity of the nitrogen gas required to achieve this will differ with the polymer treated. The level of activation is dependent upon the time of exposure to the corona and the variables influencing the power of the corona. In the present work the level of activation may be much greater than that approached in "plant" conditions where exposures may be less than 1 second but using more powerful coronas. Other work has shown that very short exposures to air or oxygen coronas, <0.5 seconds, give little alteration to the surface chemistry whilst the wettability and autohesion, e.g. of polyethylene, have been found to increase in the same manner as produced by nitrogen coronas. In the early stages of corona treatment identical mechanisms may prevail for both nitrogen and oxygen containing gases. Distinction should be made between the effects produced by surface treatment in different plasmas. Glow discharge treatment, usually at less than 100 Torr, gives different results, e.g. CASING[13], than the corona discharge, >100 Torr, where this has been found absent.

Acknowledgement

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