THE DETERMINATION OF THE REACTION RATES, WATER VAPOR PERMEABILITY, AND ACTIVATION ENERGY FOR THERMAL OXIDATION OF LDPE FILMS

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Abstract: To understand the mechanism of degradation of plastics under environmental conditions, thermal oxidation of LDPE thin film from a single manufacturer was studied. Oxidation was carried out in a pressure vessel with control at four temperatures(22,50,70 and 80°C and at 30 and 50psi oxygen pressures. Cup tests were done to determine the permeability of water vapor across the LDPE film at 60, 70, and 90ºC. The extent of oxidation was monitored using ATR-FTIR and the carbonyl content calculated from the spectra. Bands centered at 1711 and 1735 cm^{-1} was determined resulted from the carbonyl stretches. A broad band at 3100-3600cm^{-1} is attributed to O-H stretching and the fingerprint region (<1400 cm^{-1}) shows evidence of C-O stretches. The carbonyl content and permeability to water vapor increased with temperature, oxidation time, and oxygen pressure. Water permeation is a result of the disruption of the semi-crystalline structure of the film to produce amorphous regions within which the water vapor is more permeable. This study was a step in the direction for determining a reliable model for the degradation and eventual failure of medium voltage power cables in nuclear power plants (NPPs).

I. INTRODUCTION

Medium voltage power cabling is essential for operation and safety backup systems in nuclear power plants. Over the course of their operation these cables become exposed to a variety of environmental stressors such as oxygen, temperature, moisture, and/or radiation. These stressors can reduce the lifetime of the cabling significantly over time especially when moisture is in the form of complete immersion. Generally medium voltage cables that are used in nuclear power plants (NPPs) are rated from 5 to 15kV.[1] Power cables consist of insulative layers that protect the conducting layer. These usually are made of out cross-linked polyethylene (XLPE) or ethylene-propylene rubber (EPR).[1] The jacketing material is often composed of a composite based on these and other fire-resistant polymers.

With respect to the insulation base material, many studies have looked at Low Density Polyethylene (LDPE) films and their thermal degradation and its influence on the chemical and mechanical properties for a wide range of temperatures.[1-10] The properties of the aged LDPE films have been well studied and the results are well documented. Moisture effects arise from the permeation of water vapor through the insulative layer or film. LDPE water vapor permeability as well as other volatiles has also been studied.[11-12] However, these studies have considered the degradation due to these stressors separately where there could be interrelated effects between them.

In this work, we evaluate quantitatively the influence of the thermal oxidation on the polymer surface at different oxygen exposures on the water vapor permeation. To do this, the rate of the oxidation and associated activation energy for the water vapor permeation are measured.

II. PERMEATION THEORY

II.A. General Concepts and Equations

The permeability of a gaseous or liquid component, the permeant, is a measure of its ability to move through the material that resists its passage from one side to another. It is a common quantitative measure of the barrier properties of a thin film.[12] One mechanism for the permeant to travel into the film is by diffusion. This means that the permeant dissolves into the film matrix from the higher concentration side, diffuses through the film due to the concentration gradient, and then finally moves through to the other side into an external phase. Typically, LDPE films are composed of crystalline and more permeable amorphous regions through which the permeant is believed to travel.[12]

The permeability of water vapor is determined gravimetrically using the well-established ASTM method D1653-13 and commercially-available permeation cups from *Gardner*. The rate of weight loss ($\dot{m}$, g/hr) is measured by weighing the cups at different time intervals. The calculations leading to the permeability follow the ASTM procedure.

The water-vapor transmission rate, WVT, is defined as:

$$WVT = \frac{\dot{m}}{A} \qquad (1)$$

where *A* is the exposed area of the sample. The water-vapor permeance is defined as:

$$WVP = \frac{WVT}{\Delta p_{vap}} \qquad (2)$$

and Δp_{vap} is the difference in the water vapor pressures across the thin film; this is calculated from the relative humidity on both sides of the film. The permeability of the film with thickness *L* is then:

$$P = L \times WVP = \frac{L \times \dot{m}}{\Delta p_{vap} \times A} \qquad (3)$$

Typically, the water mass-loss rate is replaced by the volume of water vapor $\dot{V}$ under standard conditions, STP, using the Ideal Gas law:

$$\dot{V} = \frac{\dot{m}}{M_w} \times \frac{RT^0}{P^0} \qquad (3)$$

where T^0 and P^0 are the standard temperature (273.15 K) and pressure (one atmosphere), respectively; M_w is the molar mass of water and *R* is the ideal gas constant (8.314 J/mol K). The final equation for the calculation of the permeability is:

$$P = \frac{L}{A \times \Delta p_{vap}} \times \frac{\dot{m}}{M_w} \times \frac{RT^0}{P^0} \qquad (4)$$

The units used for *P* are the Barrer, named after New Zealand chemist Richard Barrer:

$$1\ \text{Barrer} = 10^{-10}\ \frac{\text{cm}\times(\text{cm}^3_{STP}\text{s}^{-1})}{\text{cm}^2\ \times \text{cmHg}}$$

III. EXPERIMENTAL

III.A. Materials

Fifty-micron thick LDPE pristine films, (Goodfellow Cambridge Limited) were used for this study. The average molecular weight provided from the supplier is around 400,000 g/mol. The pristine films were cut into 10.16 x10.16cm (uncertainty of ± 1.27cm) squares, which had an average mass of 0.48± 0.06 g for the 50 μm films.

III.B. Thermal Oxidation Experiment

III.B.1. Simulation of Oxidative Environment

The LDPE films were exposed to pure oxygen in 2-L pressure vessel (Parr Instruments, 4600 series) and its temperature was controlled (Parr instruments, 4838 PID controller) under proportional-only control to avoid overshooting the desired temperature upon startup. The surrounding laboratory ambient temperature was around 22-23°C. The films were placed in the vessel and spread out so that there no films were stuck together, and the surfaces were accessible by the oxygen gas. Oxygen gas from a compressed gas tank was transferred into the vessel to induce the oxygen-rich environment. The experiment was done at 30 and 50psi oxygen pressures and four temperatures (22, 50, 70, and 80°C). WinDaq data acquisition software was used to monitor the temperature profile on the outside and inside of the vessel. The oxidation durations were done for 19 and 33 days.

III.B.2. Water Vapor Transmission

The oxidized films were then cut into circles to fit in the 12cm^2 cross section of the cups used for the permeation test (Paul N. Gardner Company Inc.). The permeation test was prepared and followed according to the wet cup test in ASTM D1653-13 for 14 days to obtain the mass loss versus time for the permeation calculation. In each experiment, it was ensured a pristine 50 µm LDPE film was run alongside the oxidized film. The permeation cups were put in an oven film side uppermost using oven temperatures of 60,70, and 90°C.

III.B.3. Fourier-Transform Infrared Spectroscopy

To determine the extent of oxidation, Attenuated Total Reflectance Fourier-transform infrared spectroscopy (ATR-FTIR), with a Thermoscientific Nicolet iS10 instrument, was used to measure the absorbances of the carbonyl bands. Pristine film was run alongside the oxidized film. For oxidation, the carbonyl band from 1700 cm^{-1} to 1740 cm^{-1} should be observed.[13-14] To measure the extent of oxidation over the whole film, three scans on each side were done giving a total of six scans for a single oxidized film. The extent of oxidation was quantified by band integrations (IGOR 6.37 software). The carbonyl group bands were integrated from 1690 to 1780cm^{-1} and those for the methyl group bands from 1320 to 1400 cm^{-1}. The carbonyl bands areas were normalized with respect to the methyl group band areas which defines the carbonyl index.

IV. RESULTS AND DISCUSSION

IV.A. ATR-FTIR Spectra

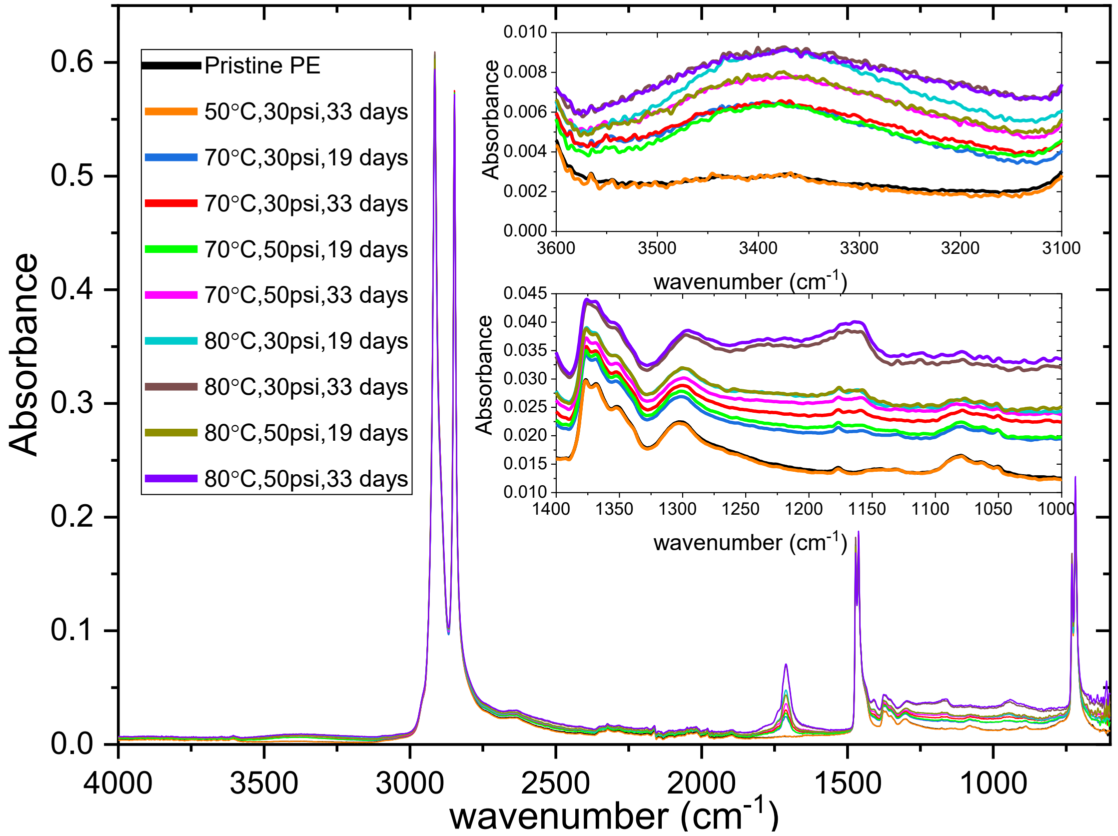


Fig. 1. FTIR spectra of the LDPE subjected to thermal oxidation in the Parr vessel at four temperatures (room temp 22, 50, 70, & 80°C) at oxygen pressures of 30psi and 50psi for 19 and 33 days. *Upper Inset:* FTIR spectra from 3100 to 3600 cm^{-1}. *Lower Inset:* FTRI spectra from 1000 to 1400 cm^{-1}.

FTIR spectra are commonly used in determining the functionality of the products formed in the surface of films.[14] Shown in Fig. 1 and its two inset plots are the spectra of interest. The carbonyl index was calculated from the spectra and it is defined as the concentration of carbonyl products normalized to the methyl C-H bands. In Fig. 1, there is a sharp band at 1711 cm^{-1} that increases as the temperature, treatment time, and oxygen pressure increases. Bands are present in the region from 3100 to 3600 cm^{-1} and from 1000 to 1400 cm^{-1}. Experimental conditions of 80°C, 50 psi of oxygen pressure, for 33 days yield absorbances close to 0.01 and greater than 0.03 for 3100 to 3600 cm^{-1} and 1000 to 1400 cm^{-1} respectively.

The increase in the broad band from 3100 to 3600 cm^{-1}`can be attributed to O-H stretches. At 3373 cm^{-1}, the absorbance takes is at a maximum. Medium bands are present in the 1000 to 1400 cm^{-1} where bands at ~1155 cm^{-1} and 1362 cm^{-1} belong to ester stretches.

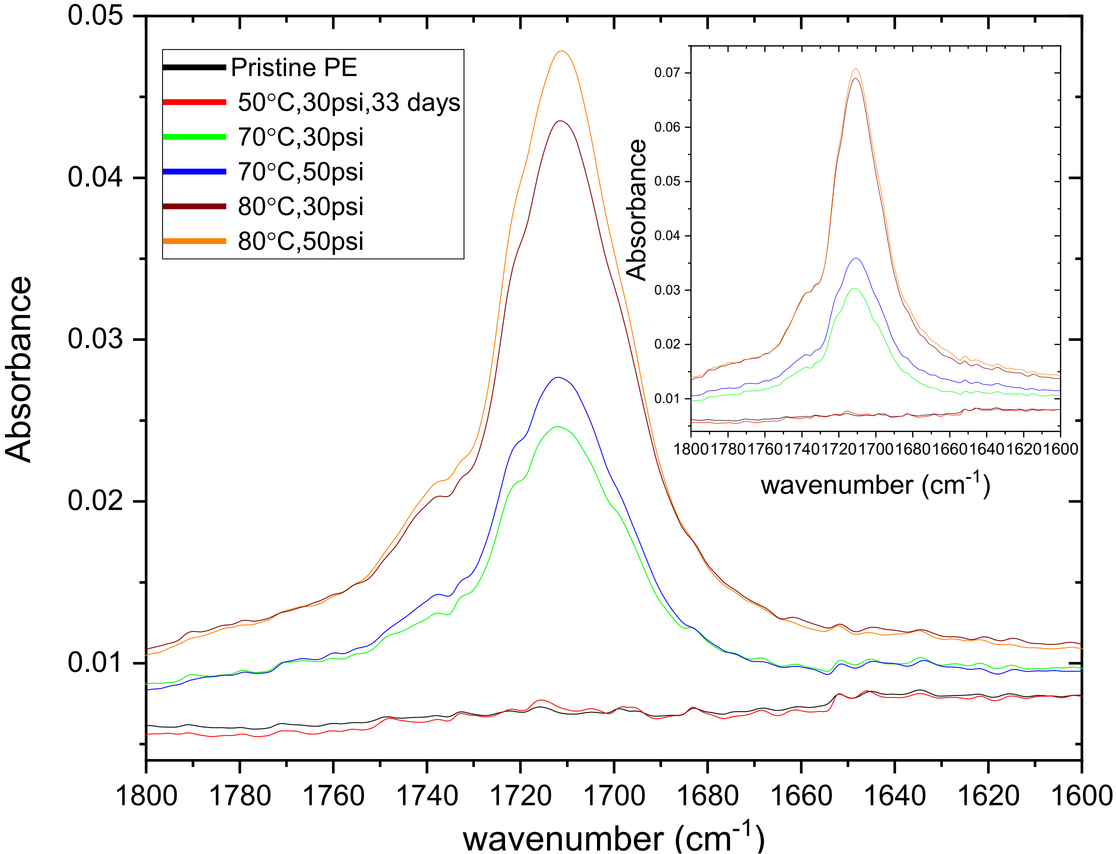


Figure 2: FTIR spectra between wavenumber 1600 to 1800 cm^{-1} responsible for the carbonyl functional groups forming on the LDPE film after 19 days of aging. *Upper Inset:* Shows the same 1600 to 1800 cm^{-1} region but for 33 days of aging. The legend applies for both the plot and its inset plot.

The strong band at 1711 cm^{-1} shown in Fig. 2 is the clear indication of carbonyl products present in the LDPE film. This band can be attributed to the ketonic carbonyl and carboxylic acid carbonyl groups formed on the LDPE film as it being oxidized and the band increases with the temperature, treatment time, and oxygen pressure.[15-16] The same 80℃ and 50 psi of oxygen pressure lead to largest absorbances which are 0.047 and 0.07 for 19 and 33 days respectively. A hump or shoulder in the band is also present. This shoulder at ~ 1735 cm^{-1} can be attributed to the formation of esters upon oxidation.[15] Another shoulder band at ~1720 cm^{-1}, belongs to the ketone, carboxylic acids, aldehydes, and esters. As the absorbances increase, the ~1720 cm^{-1} band seems to disappear. This is present when aged for 19 and 33 days as seen in Fig. 2 and the inset plot. We hypothesize that increased temperature and oxidation time allows for the more stable oxidation products to form, which are the carboxylic acid and ketone groups.[16] This is supported by Iring *et al.*, who determined that the kinetics of the aldehyde formation is very fast at high oxygen pressures and this is a secondary process.[16] From this, it can be said that as the oxidation of LDPE progresses, the ketone carbonyl groups become the dominant products are the further oxidized result of the aldehyde group products.

IV.B. Water Permeability and Carbonyl Index

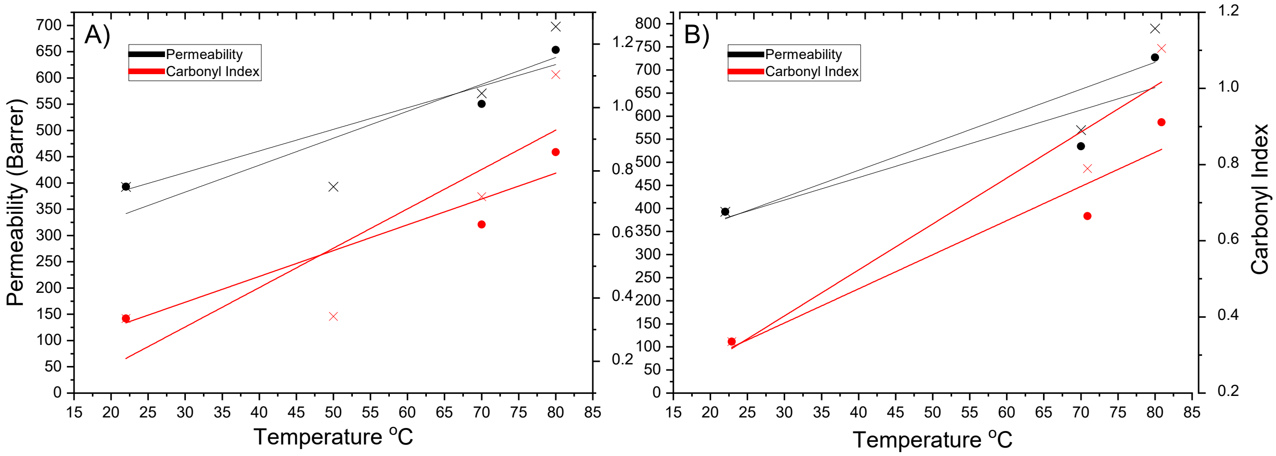


Fig. 3. Water permeability and carbonyl index values as a function of temperature for the LDPE thin films subjected to the thermal oxidation at four temperatures (room temp 22, 50, 70, & 80°C) for 19 (○) and 33 (X) days using 30psi, in *3A*, and 50 psi, in *3B*, of oxygen pressure.

The carbonyl index is the way to quantify the concentration of carbonyl functional groups in the film. As shown in Fig. 3A and 3B, both permeability of water vapor and carbonyl index (C.I.) are plotted together. The permeability increases steeply from 50 to 80°C and the same occurs with the carbonyl index for both 30 and 50 psi oxygen pressure. At 80°C and 50 psi, of oxygen pressure and treatment time of 33 days, the permeability and carbonyl index are 790. Barrer and 1.10, respectively. This can be explained by the fact that polyethylene is modeled as a semi-crystalline polymer with regions of crystalline and amorphous regions. The amorphous regions are made of polymer web-like structures where the holes represent the amorphous regions for which the gas molecules go through.[17] It has been determined that these amorphous regions serve as areas of lower activation energy for the gas molecules to permeate, as in these areas the polymer chains lack crystalline structure and therefore cannot immobilize the gas molecules from moving through the film.[17] It was also thought that the localized charged oxidized regions may act as a barrier for oxygen advancement. Though, this would require more work to better understand the mechanism of gas molecular advancement.

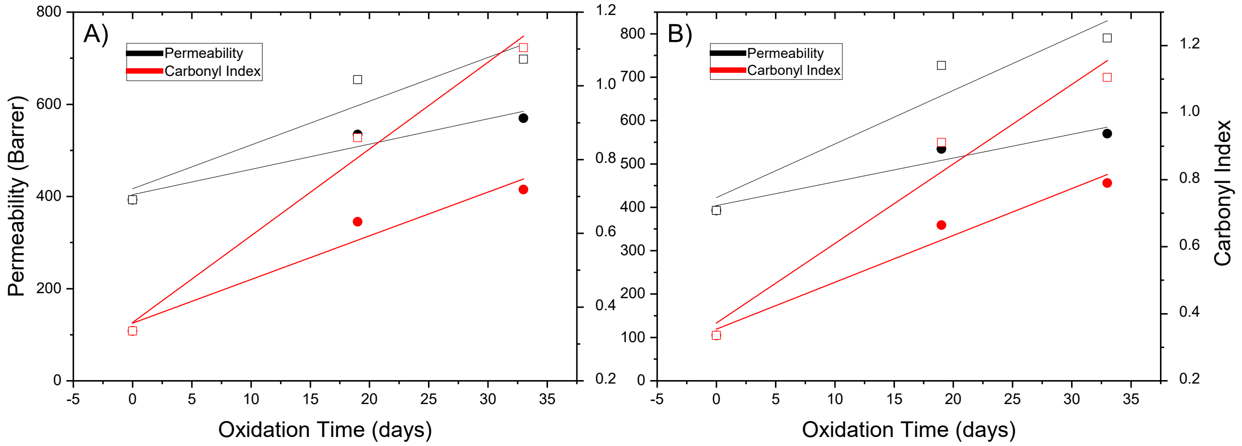
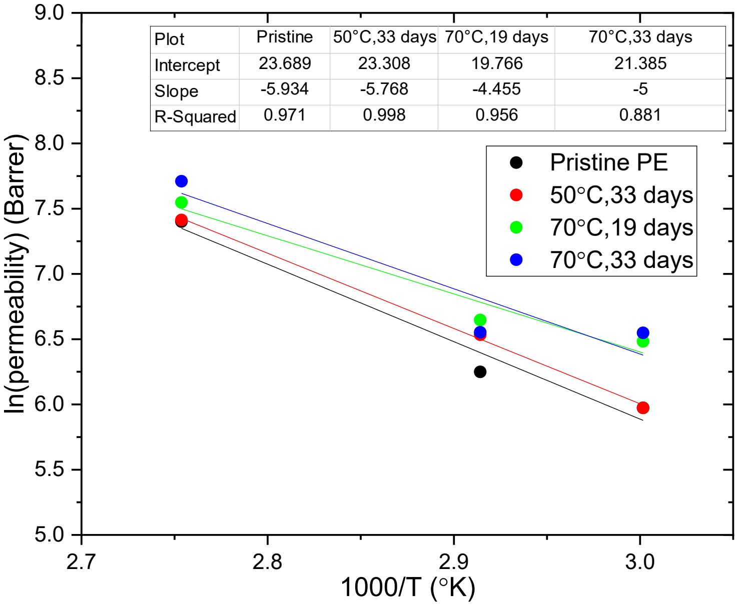


Fig. 4. Shows the water permeability and carbonyl index values against treatment time for LDPE thin films LDPE subjected to thermal oxidation at four temperatures (22, 50, 70, & 80ºC) for 19 (○) and 33 (□) days using 30psi, in *4A*, and in 50 psi, in *4B*, of oxygen pressure.

Fig. 4A and 4B shows quantitively the permeability of water vapor and the carbonyl index as in Fig 3 but now with respect to oxidation treatment time. As oxidation time increases, both quantities increase which is the same trend as seen with temperature in Fig. 3. Also, there is a dramatic increase from pristine unaged LDPE to 19 days, but less of an increase from 19 to 33 days. The same phenomenon is observed when looking at the carbonyl indexes in Figs. 4A and 4B. Looking at figure 4B for 50psi oxygen pressure, the carbonyl index increased 98.3% and 172.% from pristine LDPE to 19 days for 70 and 80°C respectively. From 19 to 33 days, it only increased 18.8% and 21.3% for 70 and 80°C, respectively. This can be explained by the fact that the polymer chain regions have reacted with the oxygen to cause regions of low activation energy and thus the chain segments would lack local order.[17] So, when temperature and treatment time increase, the chains mobilize so that they relax in a favorable thermodynamic chain structure to allow water vapor to flow through the amorphous region.



Plot	Pristine	50°C,33 days	70°C,19 days	70°C,33 days
Intercept	23.689	23.308	19.766	21.385
Slope	-5.934	-5.768	-4.455	-5
R-Squared	0.971	0.998	0.956	0.881

Figure 5: Permeability of the aged LDPE thin film done at 60,70, and 90°C for constant 30 psi oxygen pressure.

To determine an activation energy for the flow of water vapor across the oxidized LDPE films the permeability cup test must be done at different temperatures as shown in Figure 5. The calculated activation energy represents the activation energy of the water vapor moving across the film assuming Arrhenius behavior.[17] Activation energies are calculated and shown in Table 1. As the temperature and treatment oxidation times increase, the activation energy decreases. This behavior has been described for molecules with similar molecular weight as water vapor such as methane and carbon dioxide.[17]

Table 1: Shows the calculated activation energies for water vapor transport across LDPE film from Fig. 5.

Temp. (ºC)	Oxygen pressure (psig)	Oxidation time (days)	Activation Energy (J/mol)
22	0	0	49
50	30	33	47
70	30	19	41
70	30	33	37

V. SUMMARY/ CONCLUSION

Thermal oxidation of LDPE thin films was done using a Parr vessel and the extent of oxidation was monitored using the carbonyl index which is a ratio showing the concentration of carbonyl functionality produced on the LDPE film surface. The main functional groups present are O-H groups and the carbonyl groups associated with ketones, carboxylic acids and esters. It was found that increasing the temperature, oxidation time, and oxygen pressure, increased permeability and the carbonyl content. Along with this the activation energy for the process decreased, quantifying the increasing diffusion rate of water into neat PE insulation with oxidation. This gives a thorough analysis of what occurs when an oxygen-rich environment interacts with LDPE which can be a good baseline for future experiments looking at other degradation mechanisms.

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