A New Diffusion Cell for Characterizing Oxygen Permeation of Fiber Reinforced Polymers

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ABSTRACT

The gas diffusion characterization of polymers is important in many industries. For example, in the food packaging industry, it establishes the product guarantee period for food contained in hermetically sealed polymer wrapping. As a result, several methods are available for measuring gas diffusion characteristics of polymers. Unfortunately, they are not particularly suited for evaluating the much thicker polymers used in infrastructure applications such as fiber reinforced polymers. This paper describes the development of a new diffusion cell and an associated testing technique that makes it possible to characterize thicker polymer films as well as composite systems in which polymers are bonded to non-polymers such as concrete. It provides information on the background and basis of the new testing system including detailed descriptions, data collection and testing protocol.

KEYWORDS: oxygen, corrosion, permeation, sensor, quasi-steady state, diffusion/permeation cell

INTRODUCTION

Chloride-induced corrosion of steel in concrete requires the presence of oxygen and moisture for the electro-chemical reactions responsible for corrosion to continue. Repair of corrosion-damage often utilizes polymers such as epoxies or more recently, fiber reinforced polymers. The durability of such repairs depends on the extent to which these barriers can prevent entry of deleterious materials such as moisture and oxygen that allow the electro-chemical reactions to continue.

As the size of the oxygen molecule is smaller than that of the water or chloride molecule and its interactions with epoxy weaker, its diffusion characterization is the most significant. This is because the larger the molecular diameter and stronger the interactions the smaller the diffusion coefficient. For this reason, oxygen can diffuse faster than both chlorides and water.

This paper traces the development of a new diffusion cell that is geared towards oxygen diffusion characterization of polymers that are typically used in infrastructure applications. The new diffusion cell can also be used to evaluate the effectiveness of FRP-concrete systems in resisting chloride-induced corrosion.

This new diffusion cell is being used to evaluate several epoxy polymers. These can be used for repair, waterproofing, and strengthening application,
This ASTM standard covers procedures for determining the steady state rate of transmission of oxygen into packages that enclose a dry environment. Typical elements intended for this test include rigid plastic bottles, tubs or flexible bags or pouches as shown in Fig. 1 & 2.

In the test, the air inside the package is purged by maintaining a constant flow rate of nitrogen from 30 min to several hours depending on the volume of the container. Subsequently, the flow rate is reduced and maintained for the next 30 minutes before the flow of nitrogen (carrier gas) is diverted to coulometric sensors. These can count the number of electrons that enter the sensor (four electrons represent one oxygen molecule). The sensor output increases gradually before reaching a steady state that may require several hours or days. To expedite testing, the outside of the package can be maintained at 100% oxygen (see Fig. 1). This will increase the transmission rate by a ratio of 100/21 = 4.8.

Because of the dependence of the oxygen transmission rate on temperature (it varies by 3 to 9%/C), tests should be conducted in a draft-free constant temperature environment. ASTM spells out procedures for calculating the oxygen permeance of the specimen.

ASTM D3985

This ASTM standard covers procedures for determining the steady state rate of transmission of oxygen for plastics in the form of film, sheeting, laminates, coextrusions or plastic coated papers or fabrics.

Unlike ASTM F1307 where the specimen itself serves as the diffusion cell, in this set up, the test specimen is placed inside a diffusion cell where it serves as a barrier between the upper and lower parts of the cell. Precise dimensions of the cell are not specified in the standard (ASTM F1307 states that the typical diffusion cell areas are 100 cm$^2$ and 30 cm$^2$).

The volumes above and below the test specimen are not deemed to be critical. However, they should be small to allow rapid gas exchange but big enough so that a bulging (or sagging) film is not in contact with the top or bottom surfaces of the cell.

One face of the specimen is exposed to dry oxygen (test gas) while the other is exposed to nitrogen (carrier gas). A neoprene O-ring is placed in a machined groove to position the specimen on the “oxygen” face. The nitrogen side has a raised flat rim which is critical for sealing the diffusion cell when the test specimen is pressed.

Air is first purged from the upper and lower diffusion cell chambers as shown in Fig. 3. Thick samples may require several hours to purge or even overnight. After this, a reduced flow rate is maintained for 30 minutes. The sensor is then inserted and base line measurements taken. Subsequently, the test side is connected to an oxygen supply.

An equation is provided that allows the oxygen permeation coefficient to be extracted. Its unit is in mol/m.s.Pa.

Gas Chromatography

The oxygen diffusion characterization of FRP material may be determined using Gas Chromatography (GC). In an earlier study, a diffusion cell was made from an aluminum tubing (outside diameter 73 mm with a 4.8 mm wall thickness) and 114.3 mm length. An aluminum plate was welded to the bottom of the cell; FRP material was bonded to the top. Inlet and outlet tubes were attached to the bottom (Fig 4). The inlet tube was used to fill the chamber with nitrogen. The cell was kept in air where it is exposed to 20.7% oxygen. The outlet tube was used to periodically extract samples (with a 1 ml syringe) of the contents of the chamber. The composition of the extracted sample was determined using gas chromatography. Special techniques are required to extract the gas sample with the 1 ml syringe from the septum. This method was very cumbersome and error-prone since the readings were taken manually. More importantly, making the system air-tight was problematic.

CSIRO

Commonwealth Scientific and Industrial Research Organization (CSIRO) is Australia's national science agency and one of the largest and most diverse research agencies in the world. In 2001, they developed a diffusion cell to measure the oxygen characteristic of high density polypropylene membranes. These geomembranes were used to limit the amount of oxygen that would reach tailings (residues of extracted metal ores) placed in de-watered soils to prevent them from reacting with the soil and producing undesirable acid sulfate soils.

Fig. 5 is a schematic of the system developed by CSIRO. The cylindrical cell made of acrylic plastic has a volume of 18 cm$^3$ with a depth of 0.5 cm. As with the GC cell, the test specimen forms the lid of the cell where it is positioned by an O-ring to provide a gastight seal. The exposed surface area of the membrane is 39 cm$^2$.

The test assembly is conditioned for 1-2 weeks (at room temperature) in an anaerobic environment.
Subsequently it is moved to an aerobic environment. Oxygen diffusion through the membrane is measured using a Figaro oxygen sensor (KE 25)\textsuperscript{14} that is countersunk with its top flush with the base of the cell.

The Figaro sensor is essentially a lead-oxygen battery. It has a lead anode, and a gold cathode. Oxygen entering the sensor reacts to set up a current that is proportional to the oxygen concentration. Results reported indicate that it took a week for the results to stabilize. Samples tested ranged in thickness from 0.75 mm to 7.2 mm. An analytical model was developed to determine the oxygen diffusion coefficient.

**DEVELOPMENT OF DIFFUSION CELL**

The goal of the present study was to develop a new system that could be used to evaluate the oxygen diffusion characteristics of thicker polymer films used in infrastructure applications.

Previous experience with the development of gas chromatographic technique had indicated the importance of electronic data collection and the avoidance of leaks. Moreover, since a large number of tests had to be conducted, assembly of the cell had to be rapid and simple yet leak proof.

Aluminum had been used for fabricating the diffusion cell developed earlier primarily because of its light weight. However, as leaks were detected in the aluminum weld it was decided that the new cell would be made of stainless steel and would be assembled using bolts.

A pair of blank, round, stainless steel plates was purchased from Nor-Cal. The plates were 11 mm thick and had a 144 mm outside diameter. They were provided with eight bolt holes located symmetrically around the outside perimeter.

The central part of the plates was machined to create 83 mm diameter and 4.5 mm deep recess that constituted the diffusion chamber. In case the time taken to complete the test was inordinate, the volume of this chamber could be reduced by placing appropriately sized aluminum inserts in the opening.

The polymer specimen is positioned between two 144 mm diameter stainless plates. Originally, grooves were cut so that O-rings could be used to make it airtight as was used in the CSIRO diffusion cell. However, after extensive testing it was discovered to be unreliable. The problem was easily overcome by replacing the O-rings by 3 mm thick red rubber gaskets. Ironically, this had been recommended in a doctoral dissertation published over 40 years earlier.

The diffusion cell is assembled by bolting the two stainless steel plates together using eight stainless steel bolts, nuts and washers. A special, calibrated digital torque wrench was used to ensure uniformity in the applied force. As the lengths of the bolts can be varied, it provides a simple yet effective means for testing samples of different thicknesses.

**Concentration Gradient**

The diffusion cell was assembled in air and therefore one face of the specimen has the same oxygen concentration as air (20.7% of oxygen). The other face was flushed with 100% concentration oxygen to provide the needed concentration gradient. A similar gradient could also have been created by flushing pure nitrogen instead.

**Leak Proofing**

In any cell that is assembled manually, elaborate procedures are needed to ensure that there are no leaks. In this case, threaded inlet and outlet openings in the bottom plate were made leak proof by using liquid threaded seal Teflon in conjunction with a Swagelok male connector.

**Data Collection**

The same Figaro electrochemical oxygen sensor used in the CSIRO was also used in this study. However, all data was corrected to account for oxygen that was consumed by this sensor.

The sensor was connected to the Agilent 34970A data acquisition system to allow data to be recorded. Temperature data were also recorded at the same time since the diffusion coefficient depends on temperature.

Fig. 6 shows a photograph of a prototype diffusion cell with the oxygen sensor attached at the top. The bolted assembly and the rubber gasket can be clearly seen. Two cells are shown since in the testing an additional cell with an impermeable material such as steel was tested simultaneously. This set up served as an early warning system for possible leaks.

**Testing Procedure**

Following extensive trials, the set up shown in Fig. 6 was revised to incorporate an additional sensor at the bottom. This permitted the oxygen concentrations on both surfaces of the test specimen to be continuously monitored thereby enabling verification of steady state conditions assumed in the theoretical model. A schematic of the new test set up is shown in Fig. 7.
In order to make sure that the data were correctly obtained, four specimens were simultaneously tested. Three contained test specimens; the fourth had a stainless insert where no oxygen was consumed by the sensor. This set up enabled allowed any experimental errors to be readily detected.

Time for Test

Typically, results were obtained within 24 hours. The theoretical model developed allowed the permeation coefficient of the specimen to be obtained by numerical solution of the governing differential equation. Results obtained were in good agreement with those in the published literature.

SUMMARY AND CONCLUSIONS

Available methods for determining the oxygen diffusion permeation characteristics for thicker polymers used in infrastructure applications are unsuitable. This paper describes the development of a new diffusion cell suitable for this application. The diffusion cell proposed is relatively simple to construct and since bolts are used its size can be readily altered to accommodate a wide range of specimens.

Calibration tests conducted on thin polymers for which results are available validate the test method and the theoretical model developed. More tests are currently in progress to evaluate different epoxies and fiber reinforced polymers.

The diffusion cell developed provides a simple method for identifying materials and systems that are most effective for corrosion repair of infrastructure elements. By incorporating these materials it will become possible to optimize the performance of polymer materials used for corrosion repair in the future.

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REFERENCES


FIGURES

**Fig 1 – Typical Method for Attaching Plastic Bottle/ Tub**

![Fig 1 – Typical Method for Attaching Plastic Bottle/ Tub](image1)

**Fig 2 – Typical Method for Flexible Pouches**

![Fig 2 – Typical Method for Flexible Pouches](image2)

**Fig 3 - Practical Arrangement of Component ASTM D3985**

![Fig 3 - Practical Arrangement of Component ASTM D3985](image3)

**Fig 4 – Gas Chromatography Diffusion Cell**

![Fig 4 – Gas Chromatography Diffusion Cell](image4)
Fig 5 – CSIRO schematic of diffusion apparatus

Fig 6 – Prototype Diffusion Cell

Fig 7 – Illustration of Components