POLYMER TESTING

Short Communication: Material Behaviour

Application of constant volume − variable pressure (time-lag) method to measure oxygen gas diffusion through polypropylene pipes

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ABSTRACT

In this study, we have successfully applied constant volume − variable pressure method to measure oxygen gas diffusion coefficient of polypropylene-*co*-ethylene random copolymer pipes on the bases of Fick's laws of diffusion in cylindrical coordinates. Results showed that oxygen diffusion coefficient of polypropylene-*co*-ethylene random copolymer in the form of extruded plastic pipe is significantly different from thin films and sheets, mostly due to differences in plastic fabrication process yielding different orientation and crystallinity. Furthermore, long term oxygen diffusion coefficient of polypropylene pipes depends on the type of aging that the polypropylene pipes exposed during its service life. Oxygen transmission rate of single layer polypropylene pipes found higher than permissible value specified in building standards.

1. Introduction

Polyolefins have become one of the widely used plastics as a corrosion and chemical resistant material for fluid conveying systems either as a solid plastic pipe structure or as a coating layer of metal pipings. Polyethylene (PE) pipes have found significant use in water and natural gas distribution networks, whereas polypropylene (PP) pipes mostly used for hot water circulation systems at both home plumbing and industrial applications.

Temperature, impact and hydrostatic pressure resistance are the main design criteria of engineering calculations for short and long term performance evaluation of polyolefin pipes. Oxygen gas diffusion from surrounding atmosphere in to the liquid flowing inside the pipe is another design criteria not for the pipe itself but for the system itself, since dissolved oxygen gas is an important phenomena as a cause of corrosion in metal pieces, circulation pumps and heating elements [1] especially home plumbing and heating systems. Therefore many activities are ongoing to develop multilayer plastic pipe solutions having low oxygen diffusion from the surrounding atmosphere. The design

principle of these multilayer pipe products lays on a five layer structure which consists of a core pipe to hold the internal pressure, most of the time being PE, PEX (cross-linked PE) or PERT (Polyethylene of Raised Temperature), a co-extruded or coated layer of oxygen barrier material, which is either a thin layer of poly(ethylene-*co*-vinyl alcohol) (EVOH) [2] or an aluminum sheet, bonded to the core pipe with an adhesive layer that consists of maleic anhydride grafted polyethylene (MAH-*g*-PE), and finally an external layer to protect the barrier layer from external scratches and moisture. For polypropylene based plastic pipes, an aluminum layer is used as an absolute barrier to oxygen gas diffusion, as well as a structure to prevent thermal expansion of the pipeline when subjected to elevated temperatures. However, due to the high cost of aluminum sheet, alternative products are commercialized or underdevelopment to replace the aluminum layer with polymer based composites, such as glass fiber filled polypropylene or polypropylene nanocomposites. Nevertheless, one needs to know the oxygen diffusion coefficient of polypropylene and its composites in the form of plastic pipes to be able to evaluate the performance of new monolayer or multilayer pipe structure against its alternatives.

Constant volume − variable pressure (time-lag) method is one of the commonly used gas diffusion measurement methods [3], mostly preferred because of being independent of gas type and

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ability to measure non-steady state phase of the diffusion which eventually gives the gas diffusion coefficient [4]. However, the time-lag method, as all other gas diffusion test methods [5,6], is mostly employed for polymers in the form of very thin films and sheets [7]. Regardless of test method, gas diffusion through polymers in the form of thick wall plastic pipes are rarely studied and reported [8].

Oxygen gas diffusion coefficient of polypropylene has been reported in the literature in the range of 0.58×10^{-11} m^2/s up to 1.59×10^{-11} m^2/s depending on the orientation, the specimen thickness and specimen preparation method, i.e. injection molding, cast film extrusion or compression molding [9–15]. Almost all reported studies regarding oxygen transport properties of polypropylene and its blends or nanocomposites are based on either film or membrane samples. According to the published data, it is obvious that thickness, process history and crystallinity of the specimen affects the gas diffusion coefficient of polypropylene. Hence, reported gas diffusion coefficients for polypropylene in the form of thin films may significantly differ from the polypropylene in the form of thick pipes. Therefore, experimental determination of oxygen diffusion coefficient of polypropylene in the form of plastic pipes is necessary for better engineering design of piping systems.

To the best of our knowledge, the oxygen gas diffusion of polypropylene random copolymer in the form of thick walled plastic pipes has not yet been reported. In this paper, we aimed to show the applicability of constant volume − variable pressure method to measure oxygen gas diffusion coefficient of pristine and artificially aged polypropylene pipes and reported the diffusion coefficients obtained from the experimental results.

2. Experimental

2.1. Materials

Polypropylene pipes having 20 mm outer diameter and 3.4 mm wall thickness were produced my melt extrusion from a commercial polypropylene-*co*-ethylene random copolymer material (Vestolen P 9421, SABIC Europe B.V.) with an ethylene content of 4%, isotacticity of 98%, density of 0.898 g/cm^3 and melt-flow of 0.3 g/10 min at 230 °C and 2.16 kg load as per ISO1133. A conventional single screw extruder with diameter of 60 mm and length to diameter ratio (L/D) of 30 was used at a temperature profile of 180 °C −230 °C. These pipes were cut into 1 m lengths and kept at room temperature for one week after the pipe extrusion process and labeled as PP-R. Some of these pipes were aged via hydrostatic pressure and temperature cycling as described elsewhere [16] and labeled as PP1000P and PP1500C respectively.

2.2. Measurement of oxygen diffusion coefficient

Gas transfer through a polymeric structure at a given surface area is a function of concentration gradient of diffusing gas as given in the Fick's law of diffusion (Eq. (1))

$$J = -D\frac{dC}{dx} \tag{1}$$

where J is the mass transfer rate, mol/m^{2}s, C is the concentration of diffusion substance, mol/l, x is the diffusion path (m), and D is the diffusion coefficient m^2/s. Here, it is assumed the diffusion coefficient is independent of gas concentration and is a function of temperature complying to Arrhenius law as in Eq. (2).

$$D = D_0 \exp\left(\frac{E_d}{RT}\right) \tag{2}$$

where D_0 is the pre-exponential factor, Ed is the activation energy of diffusion (kJ/mol), T is temperature and R is the gas constant.

It is assumed that gas molecules can diffuse through free volumes at amorphous phase of a semi-crystalline material and no gas diffusion takes place in the crystalline phase [17]. Therefore a decrease in gas diffusion is expected with increasing crystallinity and density [18,19]. But amorphous chain mobility is another determining factor of gas diffusivity in polymer structures by forming transport channels between free volumes [15]. For a semi-crystalline material such as polypropylene, the diffusion coefficient is related to the diffusivity of amorphous content (D_a) as given in Eq. (3)

$$D = \frac{D_a}{\tau\beta} \tag{3}$$

where β represents the chain mobility and τ is tortuosity factor [20].

At most of the studies, differential solution of Eq. (1) is done according to the Cartesian coordinates assuming the gas diffusion takes place only at one direction (perpendicular to the surface) as polymer films and sheets have parallel surfaces where diffusing gas enters and exits. However, using this simplified solution for the samples having cylindrical coordinates where the surfaces have a curvature and different surface areas at inner and outer side, can cause significant errors on determining diffusion coefficient [21]. Differential solution of the Eq. (1) in cylindrical coordinates is given in Eq. (4) with the assumption of the diffusion takes place only at radial direction [22];

$$\frac{\partial C}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) \tag{4}$$

where r is the radius of the cylinder. The complex differential solution of this equation for the gas concentration, C, is given as in Eq. (5) by Rutherford and Do [23].

$$C = \frac{C_0 \ln\left(\frac{r_c}{r}\right)}{\ln\left(\frac{r_c}{r_0}\right)} + \pi\sum_{n=1}^{\infty}\frac{C_0 J_0(\alpha_n r_c)J_0(\alpha_n r_0)U_0(\alpha_n r)}{J_0^2(\alpha_n r_0) - J_0^2(\alpha_n r_c)}\exp\left(-D\alpha_n^2 t\right) \tag{5}$$

by using boundary conditions of;

$C(r_0,t) = C_0$, concentration of gas at the inner surface of plastic pipe is constant
$C(r_c,t) = 0$, concentration of gas at the outer surface of plastic pipe is zero.
$C(r,0) = 0$, concentration of dissolved gas in the plastic pipe wall at the beginning is zero.

where (r_0) and (r_c) are respectively inner and outer radii of the plastic pipe and where U_0 is defined as $U_0(\alpha_n,r) = J_0(r\alpha_n)Y_0(r_c\alpha_n) - J_0(r_c\alpha_n)Y_0(r\alpha_n)$, J_0 and Y_0 are zero order Bassel functions of first and second kind respectively and α_n is defined as the positive root of $U_0(\alpha_n,r_0) = 0$.

The amount of gas, Q (mol), diffused from the surface of a unit pipe length to the opposite surface of the pipe can be calculated by integrating the Eq. (6).