

## Studies of diffusion of byproducts formed by the peroxide-induced cross-linking of polyethylene

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### ABSTRACT

Molecular simulations were performed to study the solubility and diffusion process of penetrant molecules in polyethylene. It was found that the solubility is governed by interplay of entropic and energetic factors. The void fraction dependence of the diffusion coefficients is consistent with the free volume theory. Diffusion of byproducts such as methane formed during the peroxide-induced cross-linking of polyethylene was found to decrease in the presence of cross-links. In practise, methane mobility is not much affected by the cross-linking. Molecular simulation is a powerful tool for cable industry to understand the diffusion of byproducts during the whole cable life.

### KEYWORDS

Polyethylene; Molecular dynamics simulation; Monte Carlo simulation; Adsorption; Degassing.

### INTRODUCTION

The cross-linking of polyethylene chains leads to significant improvements of material properties [1]. For example, when using cross-linked polyethylene (XLPE) as cable insulation, it is possible to achieve a better thermal performance compared to the untreated sample. One of the most common methods of cross-linking is the free-radical cross-linking initiated by peroxide. During this cross-linking process, however, unwanted byproducts such as methane are released. The process whereby these byproducts are removed is termed as degassing. Methane is usually removed because of safety issues due to its flammability, while the removal of other byproducts such as cumylalcohol and acetophenone is required to improve dielectric performance. In general, the temperatures used in the degassing chamber can range between 50 and 70°C.

The transport diffusivity is of great fundamental importance in applications like degassing where mass transfer plays a major role [2]. The degassing process can be described using Fick's Law:

$$\frac{\partial C}{\partial t} = \rho D \nabla^2 C \quad D = D_0 e^{-E_D/RT} \quad [1]$$

where  $C$  denotes the concentration of the byproduct at time  $t$  and position  $x$ ,  $\rho$  is the density of the material,  $D$  is the diffusion constant at temperature  $T$ ,  $D_0$  is a prefactor,  $E_D$  is the activation energy, and  $R$  denotes the universal gas constant.

Molecular simulations allow us to visualize and analyze materials at very small length and time scales related to molecular interactions that are relevant for the diffusion process [3]. These simulations can accurately predict both

macroscopic properties such as solubility and diffusion, and microscopic properties such as pore structure. Monte Carlo (MC) simulation is a statistical method for investigating equilibrium thermodynamic properties and thus does not allow explicitly assessing transport properties of particles. This approach is well suited to quantify the adsorption in porous materials. Computations are carried out in the grand canonical statistical ensemble by imposing chemical potential  $\mu$ , volume, and temperature. Molecular dynamics (MD) simulations allow one to assess the dynamic properties of the system. The system's evolution over time is simulated by integrating Newton's equations of motion giving the positions, velocities, and accelerations of all the individual atoms in the system.

The research program is to understand, at the molecular-level, the adsorption and diffusion behaviors of, e.g., byproducts formed during the peroxide-induced cross-linking of polyethylene. This fundamental understanding will help further mathematical modeling of the diffusion process of byproducts for cables in the vulcanization tube, the cooling tube, the degassing chamber, and in the operation. In this paper, models were built to simulate solubility and diffusion process of, e.g., methane in completely amorphous polyethylene.

### SIMULATION MODEL AND METHOD

MC and MD simulations were carried out using RASPA [4] and LAMMPS [5] simulation packages, respectively, in the temperature range of 27 to 327 °C. The model system is composed of 5 flexible polymer chains, each having 1000 carbon atoms on the backbone. In all our simulations, a united atom representation was used for CH<sub>4</sub>, CH<sub>3</sub>, CH<sub>2</sub>, and CH groups. The transferable potentials for phase equilibria (TraPPE) force field [6] was used in this work. All monomers are assumed to interact via Lennard-Jones potential and the connectivity of the bonded monomers is maintained by the harmonic potential. In addition, bending and dihedral energy terms were considered. The charged atoms interact with each other via the classical Coulomb potential. We employed periodic boundary conditions in all directions and the charges were treated explicitly using Ewald summation. Random links were formed between two carbon atoms to mimic the cross-linking process. The cross-linking degree is defined as the ratio of the number of cross-linked units (CH) to the total number of monomer units (CH<sub>2</sub>) in the non-cross-linked polymer. In the present study, five penetrant species (helium, nitrogen, oxygen, methane, and propane) were investigated.

The pore volume was calculated using the Poreblazer software [7]. It represents the internal free space of the polymer material accessible to a probe molecule. To