Measurement 46 (2013) 4206–4225

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

QSPR prediction of the solubility of CO_2 and N_2 in common polymers

Karim Golzar [a], Sepideh Amjad-Iranagh [b], Hamid Modarress [a,*]

[a] Amirkabir University of Technology, Department of Chemical Engineering, No. 424, Hafez St., Tehran, Iran
[b] Department of Chemistry, Amirkabir University of Technology, Tehran, Iran

ARTICLE INFO

Article history:
Received 15 October 2012
Received in revised form 31 July 2013
Accepted 6 August 2013
Available online 22 August 2013

Keywords:
Solubility
Quantitative structure–property relationship (QSPR)
Genetic function approximation (GFA)
Artificial neural network (ANN)
Adaptive neuro-fuzzy inference system (ANFIS)

ABSTRACT

In this work, a quantitative structure–property relationship (QSPR) model is presented for solubility prediction of carbon dioxide and nitrogen in polyethylene, polypropylene, polystyrene, polyvinyl acetate and poly(butylene succinate) at different temperatures and pressures. The five most important descriptors which are related to the structure of the gas molecules and the repeating unit of polymers were selected by means of a genetic function approximation (GFA) from a set of more than 1600 descriptors. The selected descriptors in addition to the temperature and pressure were used as the inputs for the artificial neural network (ANN) and adaptive neuro-fuzzy inference system (ANFIS) models to develop the required non-linear relationships. These non-linear models were assessed by some internal and external validation methods. The obtained results indicated the excellent ability of ANN and ANFIS for prediction of solubility of gases in polymers.

1. Introduction

In past decades, polymers materials such as polymeric foams have become an essential part of daily life and they are widely used as heat insulators, food trays, and support materials. The useful features of these materials are due to low thermal conductivity, light weight, and high impact strength. Formerly, these materials were produced from CFC-11 (trichlorofluoromethane) and CFC-12 (dichlorodifluoromethane) as physical blowing agents, but these gases can damage the ozone layer of atmosphere and so their production is prohibited and other gases such as carbon dioxide and nitrogen are being considered as new environmentally benign alternative blowing agents. Therefore, to design the effective procedure to construct polymeric foams with desirable characteristics information related to solubility of gases in polymers are necessary [1–8].

Various experimental techniques, thermodynamic models and prediction methods are available to evaluate the solubility of gases in polymers [3–10]. Some researchers have measured the solubility values of gases in polymeric materials, experimentally, by means of laboratory equipments. Raharjo et al. [11] measured solubility of pure and mixed gases n-C_4H_{10} and CH_4 in poly(dimethylsiloxane) (PDMS) at temperatures ranging from −20 to 50 °C. In another work Ribeiro Jr and Freeman [12] measured the sorption of mixed gas CO_2/C_2H_4 with different molar percent of CO_2 onto a cross-linked poly(ethylene oxide) copolymer which was produced by photopolymerization of a solution containing 70 wt.% poly(ethylene glycol) methyl ether acrylate (PEGMEA) and 30 wt.% poly(ethylene glycol)diacrylate (PEGDA), at temperatures ranging from −20 to 35 °C and operating pressures up to 21 atm. They concluded that the solubility values enhanced in compare to the pure-gas, by increasing the amounts of each gas in the mixture and by decreasing the temperature.

It is difficult to measure the solubility of gases in polymers, the researchers tried to evaluate it by utilizing the

* Corresponding author. Tel.: +98 21 64543176; fax: +98 21 66405847.
E-mail address: hmodares@aut.ac.ir (H. Modarress).

0263-2241/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.measurement.2013.08.012

equations of state (EOS). There are numerous cubic and non-cubic EOSs such as Sako–Wu–Prausnitz (SWP) [9], original statistical associating fluid theory (CK-SAFT) [9], Perturbed-Chain SAFT (PC-SAFT) [9,13], Sanchez–Lacombe (SL) [9,14,15], and Simha–Somcynsky (SS) [15,16] which can be used for this purpose. For example, Chen et al. [9] predicted the solubility of N_2, C_2H_4, C_4H_{10}, iso-C_4H_{10} and CO_2 in some polymers by means of PC-SAFT, CK-SAFT, SL and SWP equations of state and they concluded that good agreement can be obtained with the PC-SAFT and SL and the efficiency of the CK-SAFT is least satisfactory. In addition, the results which were obtained by SWP were somewhat acceptable. Peng et al. [13] modeled solubility of gases such as N_2, CO_2, CH_4 and C_2H_4 in molten polymers by means of SAFT and PR. To adjust the interaction energy between the gas molecules and polymer chains in mixtures, classical mixing rules were applied by using one or two adjustable parameters and better results were obtained by this two adjustable parameter model. Aionicesei et al. [14] studied the solubility of CO_2 in poly(l-lactide) and in poly(d,l-lactide-co-glycolide) by means of Aspen Polymer Plus software with two EOSs, SL and PC-SAFT. The results suggest that both SL and PC-SAFT are reliable for predicting the solubility of CO_2 in the above mentioned polymers. Li et al. [10] investigated solubility and diffusivity of carbon dioxide in the solid-state isotactic polypropylene (iPP) by using the pressure-decay method at temperatures of 373.15, 398.15, and 423.15 K and pressures ranging from 1 to 15 MPa. Also they predicted solubility and diffusion coefficient by means of SL and Fick's second law, respectively. Sato et al. [3] measured the solubility and diffusion coefficient of carbon dioxide in poly(vinyl acetate) (PVAc) and molten polystyrene (PS) at different temperatures and operating pressures by applying magnetic suspension balance (MSB) and they correlated the solubility values by the SL to within an average relative deviation of 3.6 and 1.6% respectively for PVAc and PS. In a subsequent work [2], they measured the solubility of carbon dioxide in neat poly(2,6-dimethyl-1,4-phenylene ether) (PPO) and blends of polystyrene with various weight percent of PPO (25–50 wt.%) at temperatures 373.15, 427.15, and 473.15 K and pressures up to 20 MPa. They concluded the experimental solubility data with the extended dual mode sorption (EDMS) model in conjunction with SL. Li et al. [15] adopted MSB to measure solubility of carbon dioxide and nitrogen in a polylactide melt at temperatures from 180 to 200 °C and pressures up to 28 MPa and both SL and SS were applied to predict the amount of volume swelling in the polylactide/gas mixture due to gas dissolution. They also [16] investigated solubility pressure of a mixture of two gases (HFC-134a and HFC-152a) in polymer melt (PS) by using SS. The results indicated that these EOSs are capable to predict the solubility of gases in polymers as binary and ternary mixtures.

Practical measurement of gas solubility is costly, difficult and time consuming and is not possible to be carried out at all required temperatures and pressures, moreover using EOS need a complicated calculations and tuning up one or several adjustable parameters to obtain the lowest error. While this is a very time consuming task, the results cannot be usable for other similar cases and for a new case the procedure must be repeated step by step. Therefore, in recent years reliable computational prediction methods have attracted great attention. For example, by using artificial neural network (ANN) technique Mohanty [17] estimated the vapor liquid solubility of binary mixtures with an average absolute deviation of 3% for liquid phase and less than 0.02% for vapor phase mole fraction. Nguyen et al. [18] applied ANN with 8–6–7–4 network as the optimum architecture to estimate vapor–liquid equilibrium data and bubble point for ternary systems with the lowest possible error. Ahmadi [19] proposed a model based on ANN to predict asphaltene precipitation in the oil reservoir. Nasouri et al. [20] employed the ANN technique to modeling the average diameter of electrospun polyacrylonitrile (PAN) nanofibers and showed that the technique has high prediction ability. Sresungsuwan and Hansupalak [21] used ANN to develop a relationship between the polymerization conditions and mechanical properties. Fazilat et al. [22] predicted thermal degradation kinetics (TDK) of nylon6 (NY6)/feather keratin (FK) blend films by using the artificial intelligence techniques including ANN, adaptive-neuro-fuzzy-interference system (ANFIS) and radial basis function (RBF). The large number of works done by utilizing artificial intelligence techniques show that this technique can be used in various fields of science for prediction of various properties [23–27].

The properties of materials depend on their molecular structures; in order to get a highly accurate prediction of the properties a comprehensive understanding of the relation between molecular structures and the desired properties is essential. For this purpose, quantitative structure–property relationship (QSPR) can be used as a successful tools [28–38]. QSPR has been used for decades in the process of developing various scientific fields and it has the potential to provide estimates of the desired thermo-physical properties based on detailed chemical structure information [35]. Ravindranath et al. [32] used two QSPR models to study vapor–liquid equilibrium of 332 binaries systems. Godavarthy et al. [33] presented new models for the prediction of critical properties (critical temperature, pressure and volume) of organic hydrocarbons. Bai et al. [34] calculated heat of fusion of ionic liquids. Khajeh and Modarress [35–38] predicted surface tension, flash point, liquid thermal conductivity of different alcohols and flash point of esters and surface tension of refrigerants, by QSPR models.

In QSPR, different mathematical models such as multiple linear regression (MLR) [39], partial least square analysis (PLS) [40], multilayer perceptron (MLP) neural network [20,40], radial basis function neural network (RBF NN) [41], adaptive neuro-fuzzy inference system (ANFIS) [35–37,42–44], genetic function approximation (GFA) [42,43] and support vector machine (SVM) [45] could be used to construct a linear or non-linear relationship. The most attractive methods which are employed in this field are GFA, ANN and ANFIS.

In this work, linear and non-linear QSPR models are presented to predict the solubility of CO_2 and N_2 in polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl acetate (PVA) and poly(butylene succinate) (PBS) at different temperatures and pressures. To do this, after