



Effects of composition ratio on the properties of poly(vinyl alcohol)/poly (acrylic acid) blend membrane: A molecular dynamics simulation study



Qinghua Wei, Yanen Wang^{*}, Weihong Chai, Tao Wang, Yingfeng Zhang

Industry Engineering Department, School of Mechanical Engineering, Northwestern Polytechnical University, Xi'an 710072, PR China

ARTICLE INFO

Article history:

Received 3 September 2015

Received in revised form 11 October 2015

Accepted 12 October 2015

Available online 22 October 2015

Keywords:

PVA/PAA blend membrane

Molecular dynamics

Compatibility

Binding energy

Mechanical properties

Diffusion

ABSTRACT

To investigate the effect of composition ratio on the properties for PVA/PAA blend membrane, five simulation models of PVA/PAA with different composition ratios (4/0, 3/1, 2/2, 1/3, 0/4) were constructed and simulated by using molecular dynamics (MD) simulation. The effects of composition ratio on the properties for blends were elaborated from the aspects of the compatibility, mechanical properties, binding energy, pair correlation function, and diffusion of water molecules, respectively. The result of solubility parameter indicated PVA has a good miscibility with PAA, and the static mechanics analysis shows the mechanical properties and ductility are decreased with the increase of PAA content in the blend systems. Moreover, the analysis of binding energy and pair correlation function reveal the reason why the mechanical properties of systems decrease with the addition of PAA. Additionally, the analytical results of fractional free volume is inconsistent with the diffusion ability of H₂O molecules, and the diffusion ability of H₂O molecules in blend systems has the order of 4PPVA/0PAA > 3PVA/1PAA > 2PVA/2PAA > 1PVA/3PAA > 0PVA/4PAA. The main reason for this phenomenon is that the polarity effect of carboxylic acid groups (–COOH) in PAA is stronger than that of hydroxyl groups (–OH) in PVA.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Poly(vinyl alcohol) (PVA) was widely used as the polymer matrix in field of membrane [1–2] due to its good biocompatibility [3] and its excellent film forming capacities [4]. A major disadvantage of PVA as a membrane is its poor mechanical stability and water resistance. Thus, in realistic applications, we must modify it, and the modification of PVA membranes is one of the areas of particular interest in membrane science [5–7].

Blending is often used to change the properties of polymeric materials [8]. Santos et al. [9] studied the characterization of polysaccharides/PVA blend nanofibrous membranes, results showed better tensile mechanical properties when compared with PVA and PVA/CS, and resisted more against disintegration in the temperature range between 10 and 50 °C. Li et al. [10] used phase inversion method to prepare the PVDF/PVA blend hollow fiber membranes, blending with PVA cannot only improve the hydrophilicity of PVDF membrane, but also form the interface microvoid through polymer blend phase separation. David et al. [11] prepared a PSSA/PVA catalytic membrane coupled with pervaporation used in the esterification of 1-propanol and propionic acid. The membrane exhibited both high catalytic activity and selectivity to water. Yang et al. [12] prepared a microporous PVA/

PVC composite polymer membrane by a solution casting method and a preferential dissolution method. The PVA/PVC composite polymer membrane shows excellent thermal property, dimensional stability, and the ionic conductivity; it is due to the addition of secondary PVC polymer fillers. Wu et al. [13] studied the characteristic properties of the alkaline PVA/poly(acrylic acid) (PAA) polymer membranes, and the experimental results revealed that the electrochemical properties of the PVA/PAA composite polymer membranes had been greatly improved due to the appropriate incorporation of PAA in PVA. All of these researches were carried out through experiments, and a few studies were investigated by molecular simulation method. Here, we studied the structures and properties of PVA/PAA blend membranes at varying composition ratio by a molecular dynamics simulation methodology.

The molecular dynamics (MD) simulation has been confirmed to be a powerful tool for revealing the mechanism of polymer membrane systems and investigating the equilibrium and dynamic properties of polymeric microstructures [14]. For example, Pan et al. [15] applied MD simulation to analyze the effects of polymer blend ratio on the sorption and diffusion properties of penetrant molecules in the blend membranes. Ding et al. [16] employed the MD simulation to build atomistic models of RO polyamide membranes, and investigated both ion and water transport from pressure-driven. Kawakami et al. [17] investigated Nafion membranes containing various quantities of H₂O and CH₃OH by MD simulations using the force field parameters obtained from ab initio quantum-mechanical calculations. The nanoscale phase separation and the diffusion coefficients of small molecules and proton were reported.

^{*} Corresponding author at: Industry Engineering Department, School of Mechanical Engineering, Northwestern Polytechnical University, 127 West Youyi Road, Xi'an Shaanxi, 710072, PR China.

E-mail address: wangyanen@nwpu.edu.cn (Y. Wang).

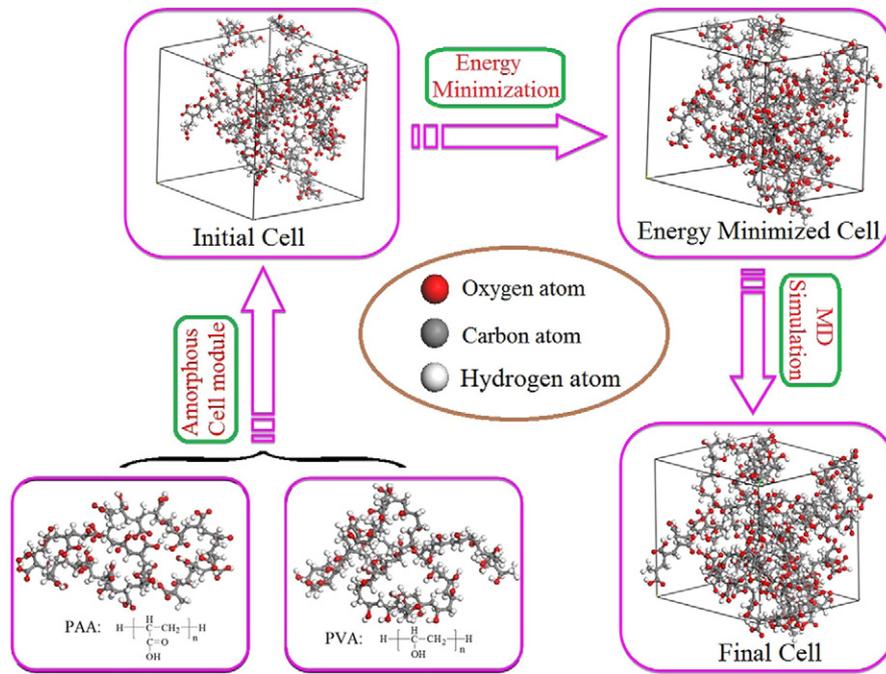


Fig. 1. Schematic diagram of amorphous cell building and its simulation. Here, the initial densities of models were set 0.6 g/cm^3 , and MD simulation procedure contains three steps: 1. NVT-MD simulation ($T = 298 \text{ K}$); 2. NPT-MD simulation ($P = 1 \text{ bar}$, $T = 298 \text{ K}$); and 3. NVT-MD simulation.

Bahlakeh et al. [18] employed MD simulation technique to elaborate the effect of degree of sulfonation on structural and dynamical characteristics of sulfonated poly(ether ether ketone) membranes at different temperatures. Tsai et al. [19] investigated the mechanical properties of graphite in the forms of single graphene layer and graphite flakes (containing several graphene layers) using molecular dynamics (MD) simulation.

Thereby, in this article MD simulation method was applied to study the morphological change process of PVA/PAA blend membrane at the molecular level. And the effects of different composition ratios for PVA/PAA blend systems on the structures and properties were investigated. Moreover, the molecular interaction mechanism between different components was illustrated from the perspective of molecular interaction. All of these provide theoretical predictions and scientific basis for formula designs of polymer membrane.

2. Materials models and simulation details

2.1. Computational models

Determination of the right chain length is critically important for the MD simulation of a polymer, since short chains might lead to end effects and cannot represent the real systems accurately, while long chains may lead to difficulties for computer simulations [20]. Thus, as the first step, PVA and PAA chains with $n = 10, 20, 30, 40, 50,$ and 60 were constructed using the Materials Studio (MS) [21]. And the carbon atoms of end groups were hydrogenated to reach saturation. Then, they were

Table 1
Detailed parameters of amorphous unit cells.

Blend system	Mass percentage of PAA	Number of atoms	Initial density (g/cm^3)	Final density (g/cm^3)	Experimental density (g/cm^3)
4PVA/0PAA	0%	1380	0.6	1.258	1.261, 1.269 [22]
3PVA/1PAA	25%	1307	0.6	1.274	1.282
2PVA/2PAA	50%	1234	0.6	1.289	1.301
1PVA/3PAA	75%	1161	0.6	1.295	1.330
0PVA/4PAA	100%	1088	0.6	1.311	1.343, 1.28 [23]

optimized (details were listed below) and piled into the amorphous units with the specified density and periodic boundary conditions.

MD simulations (details were listed below) were performed on these pure amorphous units to analyze the solubility parameters. By observing the plot of the solubility parameters changing with the number of repeat units, the right chain lengths could be determined. In order to make the models built in this paper form a strong contrast to each other, the molecular weight of PVA and PAA molecular chains would be equaled to each other. Moreover, the principle of constructing model in this study is that keeping the atomic number and molecular weight in all simulated systems similar to each other. Considering the computer resources, the atomic number of all simulated systems was taken to be about 1000–1400. Based on the atomic number and molecular weight of PVA and PAA chain, we designed five amorphous cells with the composition ratio (PVA/PAA) 4/0, 3/1, 2/2, 1/3, 0/4 for MD simulation, and each system contains four molecular chains. The amorphous models with periodic boundary conditions in this study were built at an initial density of 0.6 g/cm^3 . This low density was employed specifically to avoid ring spearing and catenation, which are due to chain rigidity and

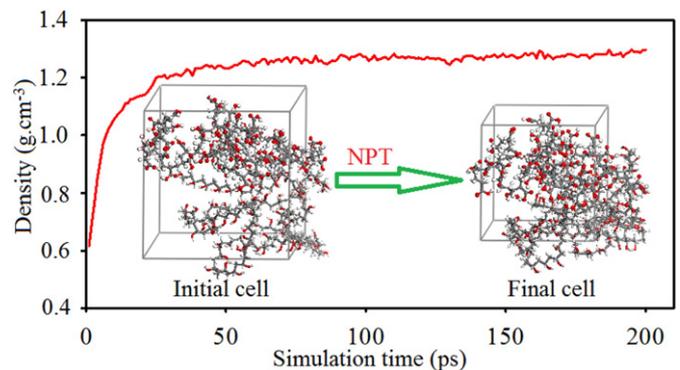


Fig. 2. The time evolution density profiles during NPT-MD simulation of 2PVA/2PAA system. The density of system was changed from 0.6 to 1.289 g/cm^3 , and the NPT-MD simulation time was 200 ps. After NPT-MD simulation, the specification of final cell becomes smaller than the initial.

Download English Version:

<https://daneshyari.com/en/article/7219912>

Download Persian Version:

<https://daneshyari.com/article/7219912>

[Daneshyari.com](https://daneshyari.com)