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Research Article

A Glass Transition Temperatures of PET and PEV Polymers Using Molecular Model Simulations with United Atoms OPLS-UA Model

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Abstract

In this study, the glass transition temperature (*Tg*) of polyethylene terephthalate (PET) and polyethylene vanillate (PEV) are obtained by molecular dynamics (MD) simulations using united atoms OPLS-UA model. The obtained *Tg* are found to be about 375K and 378K for PET and PEV polymers, respectively, which are a bit higher than those of previous experiments and computer simulation works. This imply the need of parameters optimized and validation to be fit for the specific PET and PEV systems before applied in further works of their blended systems.

Introduction

A glass transition temperature, (*Tg*), is a temperature when a polymer changes from its glassy state to the rubber state. *Tg* is used to determine the types of use of polymer, i.e., rubber-like polymers such tires for automobile vehicles have *Tg* lower than ambient temperature, while the glass-like polymers such PET bottles have *Tg* higher. Therefore, to know the *Tg* values would be helpful in the selection and design polymer materials. The polymer *Tg* could be examined by some experiments such as thermos-mechanics [1], volume dilatometry [2], spectroscopy ellipsometry (SE) [3], infrared spectroscopy (FTIR) [4], differential scanning calorimetry (DSC) [5], and dynamic mechanical test (DMA) [6]. It is believed that when the temperature of one polymer approach to *Tg*, the polymer suddenly changes its thermal properties, i.e., thermal expansivity and motions of molecule chains which can be obtained by the molecular dynamics (MD) simulation. The temperatures-dependent properties such as density, specific volume, and mean squared displacement (MSD) can be used to determine *Tg* of polymers [7]. A choice of molecular force field is very important success driver for MD simulations. If possible, the all-atoms (AA) models are most favored choice due to their ability to capture almost molecular interactions. However, the models are limited and not suitable for systems that have a huge particle number and need long simulation time like several nanoseconds or much more. The reduced degree of freedom models, then are proposed, such as the united-atoms (UA) and the coarse-grained (CG) force filed. By the way, the interactions parameters of UA and CG models are need to be verified by available experiments or simulation data based on AA forcefield model [8]. Since the biodegradable polyethylene vanillate (PEV) [9,10] polymer is like bio-based polyethylene terephthalate (PET) mimics, and has thermal properties close to PET [11], the PEV is promising to replace or blend with PET, to reduce the accumulation of PET in the environment. The ability to predict *Tg* values of PET, PEV and their blended polymers is helpful in the selection and design of blended polymers which can avoid some costly experiment works. There are some available forces fields for PET, like AA [12], UA [13] and CG [14] models. In the case of PEV, the application of AA model just recently reported [15]. In this priory study, the general force field OPLS-UA [16] parameters have been tested for obtaining the *Tg* of PET and PEV polymers, which could be help in further studies of PET, PEV and their mixtures.

Materials and Methods

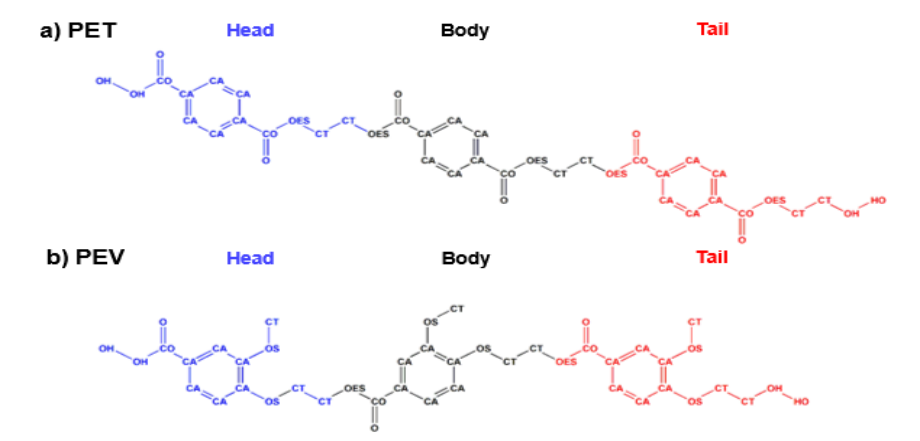

Figure 1: The corresponding OPLS-UA atom models for a) PET and b) PEV polymers.

In this study, the general force field of OPLS-UA is applied for long chains 100DP of both PET and PEV polymers. The DL_FIELD 4.1 [17] is applied for force field assignment. Since the OPLS-UA forcefield uses bond constrained model which is hard to convert with SHAKE algorithm. In this study, the harmonic bond model is applied with the same force constant parameters of OPLS-AA force field [18]. The MD simulations are performed using NPT ensemble at 1.0 atm using DL_POLY classic package [19]. The partial atomic charges are obtained averagely from the quantum optimized of their monomers, dimers, and trimers units. A polymer chain is divided into three parts, i.e., head, body and tail as shown in Figure 1. The body has assigned zero net charge, the polymer chain can be extended if desired. The time step of 1.0 fs, the leapfrog integration algorithm, and the Berendsen thermostat and barostat with relaxation times of 1.0 ps are applied. All non-bonded interactions were cut at 12.0 Å with shifted Coulombic potential correction. The systems were run until reach their equilibriums and further addition of 1.0 ns to get the average equilibrium box lengths for each temperatures, which are used to obtained the specific volume as shown in Figure 2. The increasing rate of specific volumes is obtained not constant over the temperatures. The increasing rate of trending line at high temperatures region (400K-600K) is higher than those of low temperatures region (100K-300K). The intersection of these two trending lines defined the *Tg* of polymers.

Results and Discussion

Since the main proposed of this study is searching for suitable forcefields that can applied in simulations of PET, PEV and will later use in their blended polymers, the *Tg* is mainly discussed here. The obtained *Tg* of PET and PET using the OPLS-UA are about 374K and 378K, These obtained *Tg* are some larger to available experiment data which are about 240-353K for PET [20] and 243-356K for PEV [9,21-26] and more lager than the previous computation work [15]. Note that, a small higher *Tg* of PEV than those of PET is obtained. Due to the large difference between the experimental and these calculated values of *Tg*, the OPLS-UA parameters cannot be considered adequate and not yet suitable for further calculations, e.g., *Tg* of these polymers mixtures. The parameters are needed modified and validated with experimental works or all atom models.

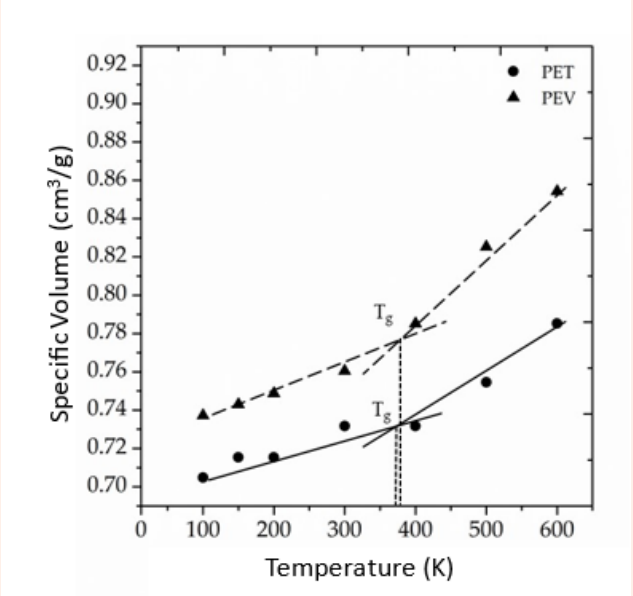

Figure 2: The obtained specific volume vs temperature for 100DP of PET (solid) and PEV (dash) with OPLS-UA model. The intersection of high and low range temperatures trended lines define the *Tg*.

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