

A REACTIVE MOLECULAR DYNAMICS SIMULATION OF HYDROLYSIS DEGRADATION IN POLYAMIDE POLYMERS

Behrouz Arash¹, Barend J. Thijssse², Alessandro Pecenko³, Angelo Simone⁴

¹Faculty of Civil Engineering and Geosciences, Delft University of Technology
Stevinweg 1, 2628 CN, Delft, Netherlands
Email: b.arash@tudelft.nl

²Department of Materials Science and Engineering, Delft University of Technology
Mekelweg 2, 2628 CD, Delft, Netherlands
Email: b.j.thijssse@tudelft.nl

³Bosch Thermotechnik GmbH, Engineering New Technologies
Junkersstrasse 20-24, 73249 Wernau, Germany
Email: alessandro.pecenko@de.bosch.com

⁴Faculty of Civil Engineering and Geosciences, Delft University of Technology
Stevinweg 1, 2628 CN, Delft, Netherlands
Email: a.simone@tudelft.nl

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Abstract

We perform reactive molecular dynamics simulations to investigate the mechanism of chemical aging of polyamide polymers by means of hydrolysis in an acidic solution at high temperature. The molecular dynamics approach is based on the ReaxFF reactive force field. The role of temperature and pH of the acidic solution on the degradation rate of polyamide polymers is studied at the nanometer scale. The simulation results show that higher temperatures and acidic condition eventuate in the breaking of more bonds within the backbone of polymer chains.

1. Introduction

Polymer materials are increasingly being used in engineering and industrial applications and are required to endure demanding service conditions for a long period. Under these conditions, reliability assessment becomes very challenging in terms of failure prediction. Predictability of failure in polymers requires understanding of their performance under environmental conditions, such as heat and chemicals, during which polymers undergo degradation of their material properties [1, 2].

Up to now, a number of experimental studies have been conducted in the literature on polymer degradation and aging [3–5]. Due to the complex physical scenario, current techniques based on testing and past experience cannot provide sufficient physical insight that is needed to fully understand polymer degradation. Another major drawback of the experimental investigations is the long time (up to several years) required to perform the tests. Therefore, the development of atomistic methods is indispensable to explore aging processes [6, 7]. Atomistic simulations enable to observe chemical reactions at the atomic level, which in turn provide a deeper insight into the mechanisms of polymer degradation. Liu et al. [8] developed reactive force field (ReaxFF) molecular dynamics (MD) simulations to study mechanisms and reaction pathways during pyrolysis of polyethylene. Their simulation results show that reaction mech-

anisms obtained from simulation trajectories are in agreement with those reported in experiments. Lu et al. [9] carried out ReaxFF simulations to investigate thermal degradation of polyimide at unphysically high temperatures varying from 2800 to 3800 K. They concluded that the activation energy and pre-exponential factor for pyrolysis of polyimide extracted from the ReaxFF simulations are yet consistent with experimental results. The hydrolysis degradation of polymer systems, however, remains poorly understood due to size and time limitations of experiments and atomistic simulations.

To address this issue, we conduct reactive MD simulations to investigate the mechanism of chemical aging of nylon 66 polyamide polymer by hydrolysis in acidic water solution. For this, a method to produce a two-layer model of the polymer and water solution is developed. Simulations are based on the ReaxFF reactive force field [10] over a range of temperature and pH of the acidic solution and provide a deeper insight into the mechanisms of the polymer degradation at atomistic level.

2. Methods

2.1. ReaxFF simulations

To study the chemical events associated with polymer degradation, we utilize the reactive force field ReaxFF [10]. This force field fairly preserves the accuracy of quantum mechanics and enables MD simulations for modeling relatively large atomistic systems. In contrast to traditional force fields for polymers, which are unable to simulate chemical reactions accompanying with forming and breaking bonds, ReaxFF allows to model bond formation/breakage. In the ReaxFF method, the overall system energy is described as [10]

$$E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{tors} + E_{triple} + E_{H-bond} + E_{vdWaals} + E_{coulomb}, \quad (1)$$

which includes bond energies (E_{bond}), lone-pair energies (E_{lp}), energy to penalize over-coordination (E_{over}) and stabilize under-coordination of atoms (E_{under}), valence angle energies (E_{val}), torsion angle energies (E_{tors}), triple bond energies (E_{triple}), hydrogen bond interactions (E_{H-bond}) and terms to handle nonbonded van der Waals ($E_{vdWaals}$) and Coulomb ($E_{coulomb}$) interaction energies. The force field parameters used in this study are taken from Ref. [11]. In the following MD simulations, the time step is set to be 0.1 fs and the Nos-Hoover thermostat and barostat algorithms [12] are used for the conversion of temperature and pressure. All simulations are performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [13], and the visualization of atomistic systems is done by OVITO [14].

2.2. Model construction

To characterize a polyamide polymer system, 24 nylon 66 chains with a predefined mass density of 1.15 g/cc are initially packed into a confined region bounded by two aluminum layers in the z-direction. The n in the nylon 66 formula (i.e., $(C_{12}H_{22}N_2O_2)_n$) is equal to 10. The size of the box is $4.3 \times 4.3 \times 5.5 \text{ nm}^3$ and periodic boundary conditions are applied along all directions. The aluminum layers are fixed in the x- and y-directions, while they are not constrained along the z-direction. In order to achieve a smooth polymer layer and to remove internal stresses in the system, molecular simulations are initialized with a geometry optimization with the convergence criteria of 0.0001 kcal/mol to minimize the total energy of the system. Once the minimization process is completed, the system is allowed to equilibrate over the isothermal-isobaric ensemble (NPT) at room temperature (298 K) and atmospheric pressure (1 atm) for 100 ps. These processes allow adjusting the volume of the system at $4.3 \times 4.3 \times 5.3 \text{ nm}^3$, and keep the aluminum layers and polymer amorphous at the equilibrium distance. Next, the aluminum layers are removed from the periodic box and a 7 nm-thick vacuum space is added to the top of the box. Finally, a layer of water solution with a mass density of 1 g/cc and a specific pH level is placed in the vacuum space as illustrated in Figs. 1(a) and 1(b). The water solution is equilibrated at room temperature and

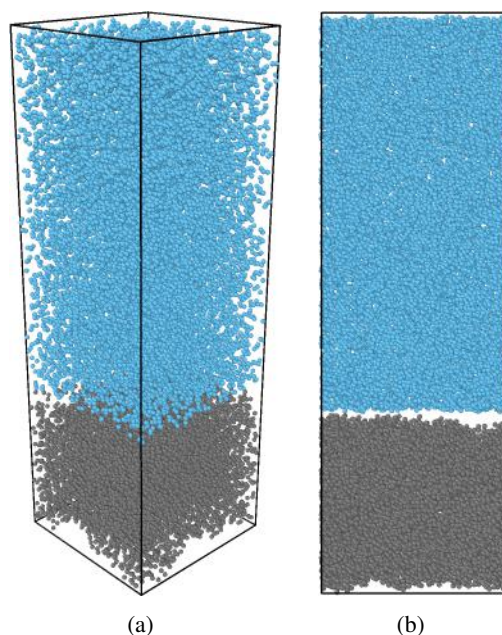


Figure 1. Two-layer model of nylon 66 polymer and water solution with a pH of 7: (a) perspective view, and (b) side view.

atmospheric pressure before adding it to the vacuum space. The role of any pH adjustment is to alter the concentration of hydronium (H_3O^+) and nitrate (NO_3^-) ions. The size of the two-layer simulation box is $4.3 \times 4.3 \times 12.3 \text{ nm}^3$ with periodic boundary conditions along x- and y- directions and mirror boundary conditions along the z-direction.

2.3. Degradation analysis

A series of simulations were performed on the equilibrated structure using constant particle number, constant volume and constant temperature ensemble (NVT) at high temperatures. It is noteworthy that although the elevated simulation temperature will probably cause some uncertainty in mechanism analysis, it can significantly reduce the simulation time. Moreover, applications of the increased temperatures in ReaxFF simulations have been shown to be well consistent with experimental observations [8, 9]. The physics behind the degradation process is as follows. Thermal degradation at high temperatures leads to the breaking of bonds within backbones of polymer chains. Moreover, the diffusion of water inside the polymer system and reactions between water molecules and polymer chains further accelerate the degradation process. The most frequent reaction pathway involved in the hydrolysis degradation is the cleavage of C-N bonds within backbone of polymer chains since the dissociation energy of these bonds is lower than C-C bonds. The cleavage of bonds is recognized using a bond order cutoff of 0.3. To quantify the degree of degradation, the number of broken C-N bonds within the backbone of polymer chains is calculated during the simulations, and a breakage ratio is defined as the ratio of broken bonds over the total number of C-N bonds.

3. Results and discussion

We first study the effect of temperature on water hydrolysis degradation of nylon 66. Fig. 2 presents the breakage ratio versus time for the polymer system illustrated in Figs. 1(a) and 1(b) at different temperatures varying from 1900 to 2200 K, while pH of water solution is fixed at 7. From Fig. 2, the rate of breakage ratio initially increases rapidly, but then approaches an value of 1. This observation can be

interpreted by assuming that the concentration of unbroken C-N bonds is high in the beginning, resulting in a great probability of bond breaking. However, after simulation time of around 100 ps, the low concentration of unbroken bonds induces a decrease in the rate of breakage ratio. It can also be seen that the breakage ratio increases with an increase in temperature. For example, the breakage ratio increases from 0.65 to 0.85 with an increase in temperature from 1900 to 2200 K at $t = 100$ ps, indicating a percentage increase of 30%. It implies that at higher temperatures carbon and nitrogen atoms within the polymer chains have greater kinetic energy to overcome the activation energy required for bond breakage. An estimate of the activation energy can be obtained by making an Arrhenius plot of the times to 50 % breakage. The result for this particular breakage condition is 0.50 ± 0.06 eV. Note that this value should be interpreted as an effective activation energy for the combined actions of water diffusion and bond breaking.

Next, we investigated the effect of pH of water solution on the breakage ratio of the polymer system in Fig. 3. The simulation temperature is set to be 2200 K and pH of water solution is adjusted to be 0 for acidic condition. In case of pure water solution with pH of 7, the breakage ratio reaches 1 after 300 ps. The time required for a complete hydrolysis degradation (i.e., a breakage ratio of 1) significantly decreases to 150 ps in the presence of the acidic condition. In addition, the breakage ratio in the acidic condition is higher compared to what is measured for pure water. For instance, the breakage ratios at pH = 7 are 0.14 and 0.54 after simulation time of 50 and 70 ps, respectively. The ratios raise to 0.49 and 0.84 at pH = 0. It implies that an acidic condition substantially accelerates the chemical reactions involved in the hydrolysis degradation process.

4. Conclusion

Reactive MD simulations were employed to investigate the mechanism of hydrolysis degradation of nylon 66 polyamide polymers. A method to produce a two-layer model of the polymer and water solution is developed. The pH of the water solution is adjusted by altering the concentration of hydronium (H_3O^+) and nitrate (NO_3^-) ions. The influence of temperature and pH of the water solution on the degradation rate of polyamide polymer is studied at the nanoscale. The simulation results reveal that higher temperatures and acidic condition lead to the breaking of more C-N bonds within the backbone of polymer chains.

Acknowledgments

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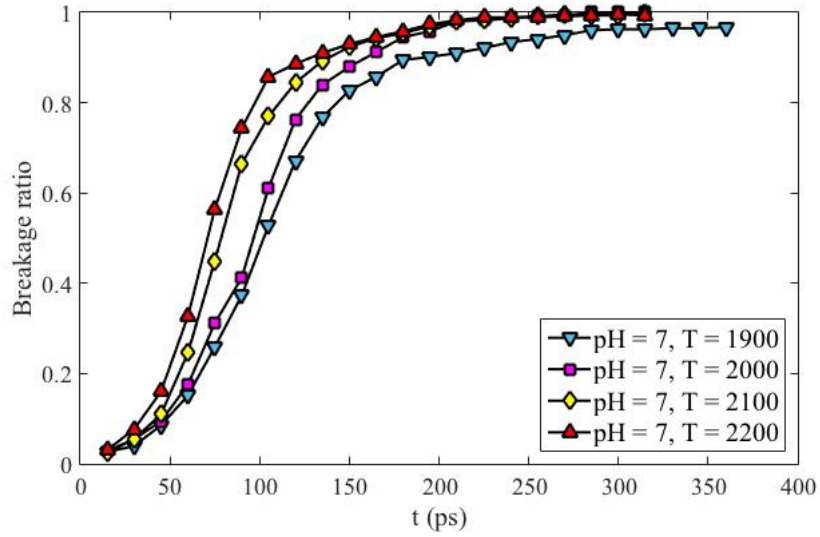


Figure 2. Effect of temperature on degradation of nylon 66.

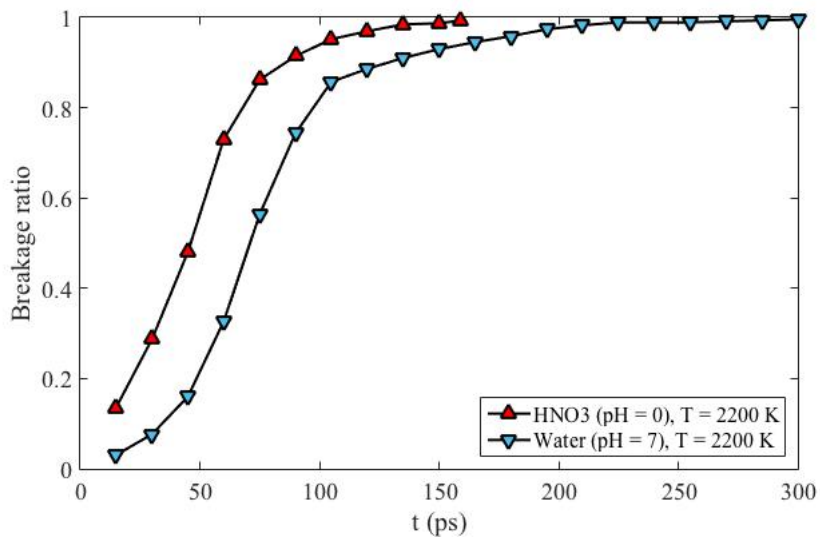


Figure 3. Effect of water solution pH on degradation of nylon 66.

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