Mechanistic Modeling of the Pyrolysis of Vinyl Alcohol Polymers

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Highlights

- The method of moments was used to track changing chain length distributions during depolymerization.
- Factors that account for the structural changes of the chains that affect kinetics are incorporated.
- The model accurately predicts low-molecular weight product yields.
- Key thermal degradation kinetic pathways were illuminated.

1. Introduction

Whether in the form of plastic articles or microplastics leaching into the environment, the mishandling of post-consumer plastic waste threatens current and future generations of life. A contributing factor to this crisis is the inefficiencies of existing recycling processes. While switching to chemical recycling via pyrolysis could be a practical alternative to reduce the amount of plastic sent to landfills, the process is not widely utilized because the product yields are difficult to tailor and not easily predicted. The uncertainty is because the thermal degradation pathways are highly sensitive to the components present in the feedstock. Therefore, a thorough understanding of the depolymerization mechanisms is necessary to reduce the unpredictability and guide optimal reactor design. As a key step towards accomplishing this, a mechanistic model was developed that can accurately simulate the depolymerization of various vinyl alcohol-containing polymers, which are commonly used in flexible and rigid plastic packaging. The model is deterministic, employing the method of moments (MoM) to track changes in length-dependent distributions of polymer chains as a function of time. Additionally, the model captures the topological changes to the backbone as hydroxyl functional groups dehydrate from the chain and implements probabilistic factors in the rate equations to account for the dependence of kinetics on structure. This model improves our understanding of the kinetics by which vinyl alcohol-containing polymers depolymerize under pyrolytic conditions, helping to move chemical recycling ahead.

2. Methods

For depolymerization systems, semi-detailed deterministic methods are often advantageous as they have lower computational costs and only lose a small level of chemical detail compared to more detailed fully stochastic methods. One promising type of deterministic model utilizes the MoM, which tracks changes in molecular weight distributions of polymer chains with respect to space-time or time [1]. In this work, each moment represents a different intensive property of the polymer. For instance, the zeroth moment is representative of the molar concentration of polymer, the first moment is the mass concentration of polymer, and so on [2]. Additionally, characteristics that can be monitored experimentally, such as the time-dependent number average molecular weight, are calculated from ratios of these length-dependent distributions [2]. Using moment-based ordinary differential equations, the evolution of low-molecular weight products can be simulated explicitly, leading to accurate predictions of pyrolysis product suites.

One limitation of this methodology is the lack of mid-chain structural information during the depolymerization process. This limitation hampers the accurate modeling of chains with temporally changing repeat unit structures, such as hydroxyl-containing compounds. Subsequently, the goal of this work was to integrate structural probabilities with the MoM to eliminate this gap in the methodology,

expanding the number of applicable polymer systems. Specifically, this study focused on two vinyl alcohol-containing polymers: polyvinyl alcohol (PVA) and ethyl-vinyl alcohol (EvOH), a prominent consumer plastic used as a barrier film in food packaging [3]. Both polymers follow a similar depolymerization mechanism, a sample of which is shown in Fig. 1, consisting primarily of (1) 1,2 dehydration, (2) Grob-fragmentation, and (3) retro-ene reactions. Fig. 1 shows how the three reactions compete for hydroxyl functional groups, the concentration of which changes throughout the depolymerization process. To accurately capture the underlying chemistry, deterministic triad and tetrad probabilities are calculated at each time step to adapt the relevant reaction rates to more accurately account for the influence that structure has on the depolymerization mechanism. A system of moment-based ODEs with probabilistic multipliers is used to track changes to the chain length-dependent distributions as well as the explicit evolution of low-molecular weight products (LMWP) and repeat unit sequences.

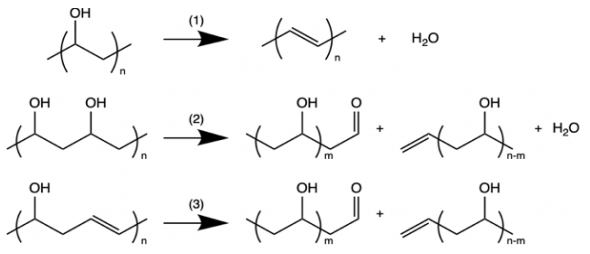

Figure 1. Sample of reactions within the model. (1) 1,2 dehydration, (2) Grob-fragmentation, (3) retro-ene.

3. Results and discussion

These models predict mass loss and specific LMWP yields as a function of temperature and time. While the models are highly detailed, the results can be consolidated to be compared against more global measures, such as mass loss (shown in Fig. 2). From this work, important mechanistic pathways were illuminated. For instance, reaction (2), which was previously overlooked by mechanisms proposed in the literature, was shown to be a vital pathway for water production and chain scission. Additionally, this work has provided evidence that the depolymerization mechanism of EvOH copolymer is directly influenced by the repeat unit composition and sequencing of the backbone. Lastly, by conducting sensitivity analyses, ideal iso-thermal and temperature ramping conditions were identified to improve the selectivity of high-value products, guiding more optimal reactor design.

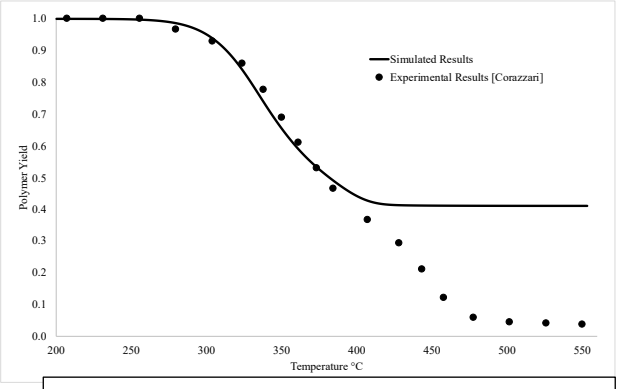

Figure 2. Comparison of experimental thermogravimetric analysis [4] and simulation results. Note that only reactions that capture the first stage of degradation are incorporated, clearly shown by the plateau.

4. Conclusions

By combining the MoM with structural probabilities, this model captures the degradation behavior of a polymer with a reactive and variable backbone structure. Additionally, these models quickly and accurately predict the LMWP distributions under various pyrolysis conditions, reducing the uncertainty surrounding the thermal degradation mechanism of vinyl alcohol-containing polymers. This work seeks to encourage further experiments and the eventual adoption of industrial-scale chemical recycling.

References

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Keywords

Polymer pyrolysis; Mechanistic modeling; Vinyl alcohol polymers; Recycling.