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The hydrolysis properties of polyethylene glycol under ambient nonthermal plasma conditions

Parsa Pishva,^a Abdol Hadi Mokarizadeh,^b Rongxuan Xie,^a Jinyao Tang,^{ib}^a
Xiaochen Shen,^a Yanlin Zhu,^a Mesfin Tsige^{ib}*^b and Zhenmeng Peng^{ib}*^a

Polyethylene glycol (PEG) has been widely used in various industries for its biodegradability. However, the biodegradation of high molecular weight PEGs poses challenges due to limited microbial uptake. In this study, we investigated a rapid nonthermal plasma-assisted hydrolysis method to break down long-chain PEGs into shorter chains and valuable liquid and gas products. Utilizing a dielectric barrier discharge (DBD) reactor under ambient conditions, we achieve complete conversion of PEG into gas and liquid products, including methane (CH₄), carbon monoxide (CO), carbon dioxide (CO₂), methanol (CH₃OH), ethanol (C₂H₅OH), acetic acid (CH₃COOH), and ethylene glycol (C₂H₆O₂), in mere minutes, which is significantly faster than conventional hydrolysis and biodegradation methods. Experimental results show that liquid products dominate throughout the reaction, while gas products increase over time, arising from secondary reactions of the liquid intermediates. Density functional theory (DFT) calculations elucidate the reaction pathways responsible for product generation. These findings highlight the promise of nonthermal plasma-assisted hydrolysis as an efficient approach for converting PEG into short-chain products and valuable chemical intermediates.

Introduction

Polyethylene glycol (PEG) which is an organic water-soluble polymer with a structure represented as H(OCH₂CH₂)_nOH has diverse applications in various industries, including the production of cosmetics, water-soluble lubricants, antifreeze agents, surfactants, plastics, and pharmaceutical preparations. It has been well documented that PEG undergoes biodegradation in the presence of bacteria, whether in aerobic or anaerobic conditions, achieved by the cleavage of ether bonds.^{1–3} However, the process of PEG biodegradation under either aerobic or anaerobic conditions reveals that the growth potential of bacterial strains is influenced by the molecular weight (*M_w*) and structural conformation of PEG molecules.^{3,4} It has been reported that the biological oxidation of PEG is inherently very slow and becomes even slower as the polymer chain length increases. This reduction continues until the polymer molecules reach a size where they cannot enter the cell, preventing degradation.^{1,5} For instance, certain studies indicate that PEGs with a molecular weight exceeding 1000 are not biodegradable.⁵ It has also been reported that various factors, including water content, pH, temperature, UV light exposure, the presence of enzymes, oxygen, and oxidants like reactive oxygen species (ROS), significantly influence the

biodegradability of PEG. As a result, PEG cannot be universally classified as biodegradable under all environmental conditions.⁶ Therefore, developing a method to efficiently decompose PEG of any chain length within a short reaction time is essential.

On the other hand, while PEG is typically regarded as nearly non-toxic, researchers have identified certain safety concerns related to both low and high molecular weight PEG.⁷ Smyth *et al.* documented chronic oral toxicity of PEG oligomer (*M_n* ~ 200) in rats, revealing adverse effects that were also observed in monkeys.^{8,9} Liu *et al.* also confirmed that PEG-1000 and PEG-4000 show moderate cytotoxicity, especially at high concentrations. This implies potential safety issues with these seemingly safe materials.⁷ Moreover, it has been reported that each PEG must be individually tested for biological effects, as these cannot be reliably predicted based solely on average molecular weight. PEGs with varying molecular weights may exhibit different levels of toxicity, highlighting the need for comprehensive testing.¹⁰ Hence, finding effective methods for the decomposition of PEG becomes crucial, particularly in situations where biodegradation is not possible.

Some researchers have explored thermal methods for the decomposition of PEG, but employing this approach requires a long time for the decomposition of PEG, especially the ones with high molecular weight. For example, Han *et al.* showed that the thermal degradation of PEG, with a molecular weight of 6000, at 80 °C, requires 1000 hours of reaction.¹¹ Glastrup *et al.* showed that the thermal decomposition of tetraethylene glycol (TEG), utilized as a model molecule for PEG, at 70 °C for

^a Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA. E-mail: zmpeng@sc.edu

^b Department of Polymer Science, The University of Akron, Akron, Ohio, 44325, USA

Therefore, in this study, we explore a novel strategy that utilizes nonthermal plasma in a dielectric barrier discharge (DBD) tubular reactor to enable the efficient nonthermal plasma-assisted decomposition of PEG in the presence of water vapor under ambient temperature and pressure conditions and investigate the effect of reaction time on the PEG conversion and yield of different products. The nonthermal plasma can produce highly reactive species from water vapor, mainly in the form of ions and radicals. These species play a crucial role in breaking the bonds within the PEG structure, resulting in a very fast reaction that can facilitate PEG decomposition compared to conventional thermal methods. On the other hand, unlike the mentioned thermal-based methods, nonthermal plasma-assisted decomposition in the presence of water vapor does not require high temperatures for efficient bond cleavage in PEG. Moreover, this method significantly reduces the probability of contamination or the addition of impurities to the final products of the reaction. Finally, to the best of our knowledge, a thorough investigation of the products resulting from the decomposition of PEG has not been undertaken; therefore, the present study thoroughly investigates all products obtained from nonthermal plasma-assisted decomposition of PEG in the presence of water vapor.

Materials

As shown in Fig. 1, the end of the DBD tubular reactor, wherein the PEG hydrolysis reaction takes place, was connected to an online Universal Gas Analyzer 300 to analyze and quantify the gas products as they are produced. The gas products were also analyzed by *in situ* Fourier transform infrared (FTIR) spectroscopy

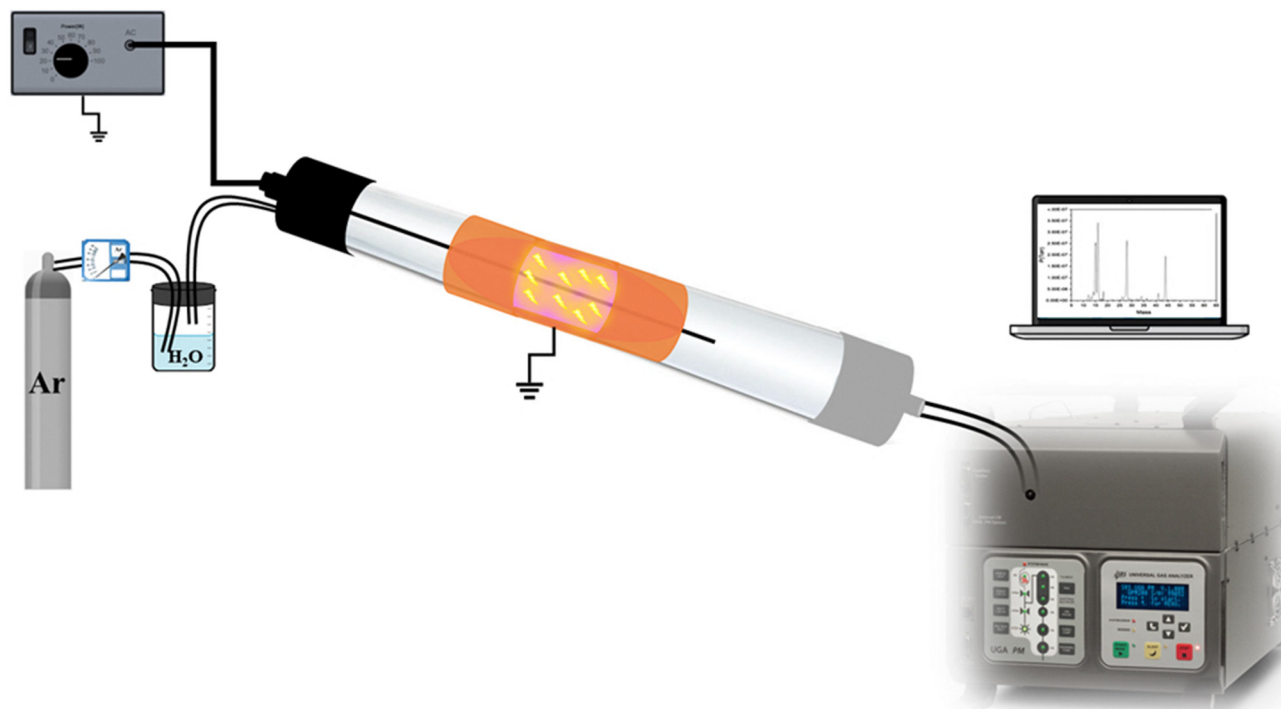


Fig. 1 Schematic of the DBD reactor system for nonthermal plasma-assisted hydrolysis of PEG.

with Nicolet 6700 IR spectrometer to confirm data obtained from the gas analyzer during plasma-assisted hydrolysis of PEG.

PEG and liquid products after plasma-assisted hydrolysis reaction were analyzed by proton nuclear magnetic resonance ($^1\text{H-NMR}$) using Bruker Avance III-HD 400 MHz. For this purpose, liquid products were dissolved in D_2O with a 10 mg ml^{-1} concentration. Next, liquid products were characterized with matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF) using a Bruker Ultraflex II MALDI-TOF/TOF instrument. Both liquid products and 2,5-dihydroxybenzoic acid, which was used as the matrix, were dissolved in acetonitrile with concentrations of 0.5 mg ml^{-1} and 5 mg ml^{-1} , respectively. $0.5 \mu\text{l}$ of liquid solution and $0.5 \mu\text{l}$ of matrix solution were dropped onto the sample plate spot and dried in air at room temperature. Positive ion MALDI-TOF MS spectra of bio-oil samples were recorded with reflectron detection mode. Accelerating voltage, laser intensity, and overall laser shots were 20 kV, 50%, and 5000, respectively. The detection range was between 500–10 000 Da.

Results and discussion

Product distribution of PEG hydrolysis

The non-thermal plasma-assisted hydrolysis of PEG yielded gas and liquid products. Fig. 2 illustrates the influence of reaction time on the yield of these products. According to Fig. 2, it is evident that all reaction times resulted in the conversion of whole PEG into liquid and gas products, except for the 2-minute reaction for which 11% of the PEG remained unreacted at the end of the reaction. These results confirm

that the non-thermal plasma method is significantly faster compared to conventional thermal methods for the hydrolysis of PEG. A longer reaction time results in a slight reduction in the production of liquid products, accompanied by a small increase in the production of gas products. This suggests that prolonging reaction time results in the initiation of secondary reactions within the initially produced liquid products during the hydrolysis reaction, facilitating their conversion into gaseous products by the cleavage of various chemical bonds within their structures, as will be discussed later. However, it should

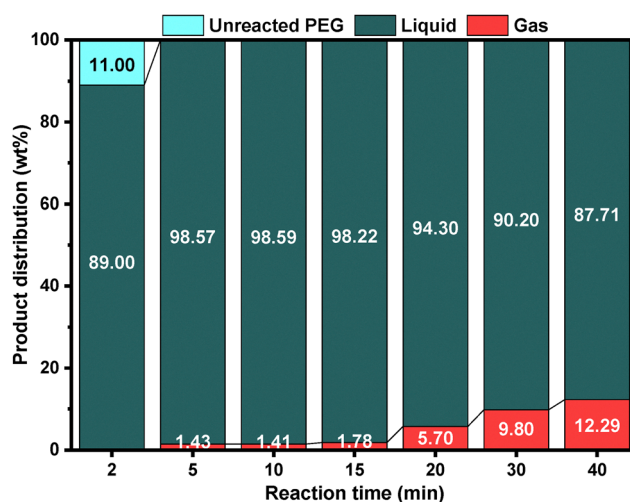


Fig. 2 The effect of reaction time on the distribution of gaseous and liquid products in nonthermal plasma-assisted hydrolysis of PEG (input power = 25 W).



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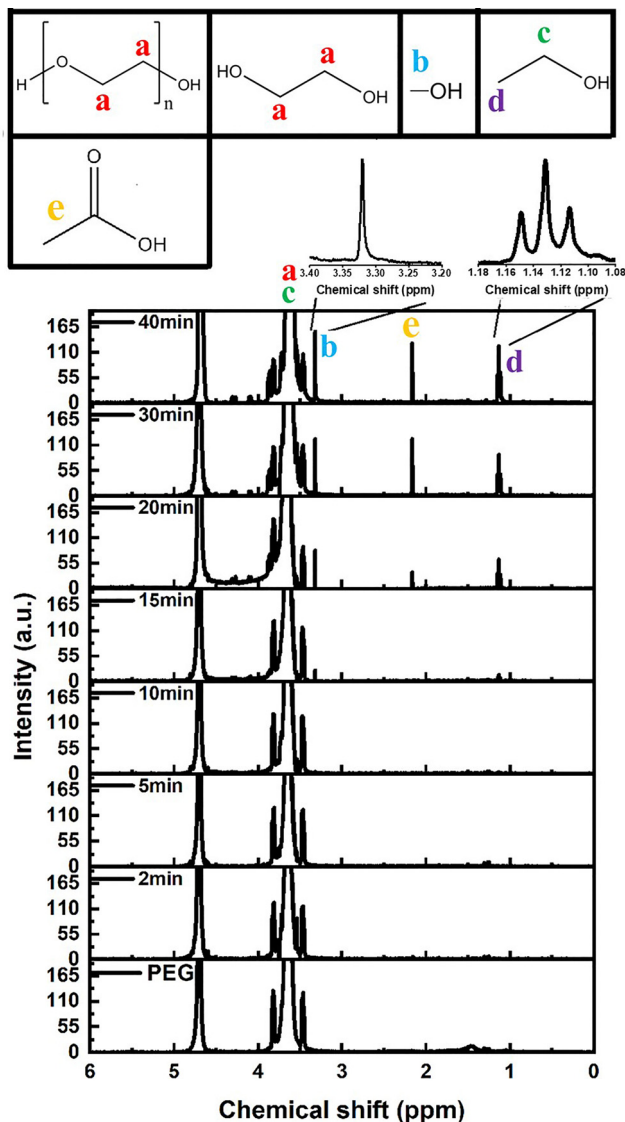


Fig. 4 The effect of reaction time on the ^1H NMR spectra of liquid products of nonthermal plasma-assisted hydrolysis of PEG.

the PEG structure are broken, leading to liquid products with chain lengths that have more uniform molecular weights compared to the original PEG before hydrolysis reaction.

Fig. S3 shows the zoomed MALDI spectra of PEG and the distance between the main peaks. As shown in this Figure, the difference between m/z values of every two adjacent main peaks is 44, which is the molar mass of ethylene oxide the monomer from which PEG is formed. This value is the same for all samples before and after the hydrolysis reaction. Therefore, it can be inferred that the bond cleavage can result in the separation of ethylene oxide monomers from PEG chains, resulting in shorter chains. Longer reaction times can break more bonds and release more ethylene oxide, resulting in shorter and lighter PEG chains.

Reaction pathway and DFT calculations

Non-thermal water plasma produces various reactive species, including hydrogen radicals ($\bullet\text{H}$), hydroxide radicals ($\bullet\text{OH}$),



Fig. 5 The effect of reaction time on the MALDI spectra of liquid products of nonthermal plasma-assisted hydrolysis of PEG.

protons (H^+), hydroxide anions (OH^-), atomic oxygen (O), and free electrons, which are considered the main reactive species generated.^{42,43} The optical emission spectrum collected during nonthermal water vapor plasma is shown in Fig. S4. Prominent emission features include peaks at 656 nm and 777 nm, corresponding to atomic hydrogen radical (H_α , $n = 3 \rightarrow n = 2$ transition) and atomic oxygen, respectively, confirming water dissociation.^{44,45} Each of these species can potentially react with PEG molecules. This study focuses on the role of $\bullet\text{OH}$ and $\bullet\text{H}$ radicals in PEG bond cleavage due to their high reactivity. To explore the reaction pathways, density functional theory (DFT) with the B3LYP/6-31++G(d,p) functional and basis set was employed to investigate possible reactions of a 5-mer PEG molecule in the gas phase. All harmonic frequency calculations were performed at a temperature of 120 °C. While more comprehensive studies are needed to fully understand the reactions of all species, these can be computationally intensive. However, we believe that our current approach and assumptions are reasonable and can contribute to a better understanding of the primary reactions responsible for PEG depolymerization. Since $\bullet\text{OH}$ and $\bullet\text{H}$ radicals are assumed to play a significant role in depolymerization, identifying the primary reaction sites in PEG is crucial for proposing the reaction pathway. Previous studies have demonstrated that $\bullet\text{OH}$ and $\bullet\text{H}$ radicals can abstract hydrogen or hydroxyl groups from the polymer backbone.^{46–49} Therefore, it is valuable to investigate the activation energy for H/OH abstraction at different sites by these radical species. Table S1 presents the

The DFT calculation results indicate that the main liquid products are ethylene glycol, ethanol, methanol, and acetic acid, aligning with the NMR findings in Fig. 4. The results also show that gas-phase products, such as CH_4 , CO , and CO_2 , primarily form from the reaction of radical species with liquid-phase products. Moreover, higher activation energies may restrict the initial formation of these gas molecules.



Conclusions

The findings from the nonthermal plasma-assisted decomposition of PEG in the presence of water vapor show significant advantages over conventional thermal hydrolysis methods, particularly its significantly faster reaction rate. The reaction resulted in the complete conversion of PEG to liquid and gas products, except for the 2-minute reaction where 11 wt% PEG remained unreacted. The time-dependent shift observed in product distribution, from liquid to gas, suggests that secondary reactions within the initial liquid products contribute to further gas production as reaction time increases. Specifically, the gas weight percentage increased from 1.43% at 5 minutes to 12.29% at 40 minutes, reflecting the progressive breakdown of liquid intermediates into gaseous products through bond cleavage. Compounds such as ethanol, methanol, and acetic acid play significant roles in generating gas products, facilitated by interactions with hydroxyl radicals generated from water vapor plasma. Analyses of liquid products *via* ^1H NMR and MALDI spectra showed significant structural changes in PEG. Notably, shorter PEG chains are formed as reaction time increases, with MALDI showing a significant reduction in *m/z* values, from 2000 to 950, confirming bond cleavage within the PEG structure. These changes yield more uniform chain lengths and molecular weights within the liquid products. Based on the proposed reaction pathway and DFT calculations, liquid products, mainly composed of methanol, ethanol, acetic acid, ethylene glycol, and short-chain PEGs start to be produced first as a result of the presence of both $\cdot\text{OH}$ and $\cdot\text{H}$ reactive species. Later, gaseous products can be formed as a result of the conversion of the ethanol and methanol, due to their reaction with $\cdot\text{OH}$, to the formaldehyde, acetaldehyde, and formic acid which can further interact with $\cdot\text{OH}$ and $\cdot\text{H}$ to yield the main gas products including CH_4 , CO , and CO_2 . Finally, it should be mentioned that the high energy consumption related to the generation of non-thermal plasma may result in increased costs. Consequently, further investigations should be done to optimize the reaction parameters and conditions, aiming to enhance the energy efficiency of this method.

Author contributions

Parsa Pishva: investigation, formal analysis, methodology, validation, writing – original draft. Abdol Hadi Mokarizadeh: formal analysis, validation, writing – original draft. Rongxuan Xie: visualization. Jinyao Tang: formal analysis. Xiaochen Shen: investigation. Yanlin Zhu: writing – original draft. Mesfin Tsige: conceptualization, supervision, writing – review & editing. Zhenmeng Peng: conceptualization, supervision, funding acquisition, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part the supplementary information (SI) and will be made available upon considerable request. Supplementary information includes gas product mass and FTIR spectra, MALDI analysis of PEG, optical emission spectra of the water vapor nonthermal plasma, and DFT-calculated results. See DOI: <https://doi.org/10.1039/d5ya00163c>.

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