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POTENTIAL OF ULTRASONIC IRRADIATION IN POLYURETHANE DEGRADATION IN DEEP EUTECTIC SOLVENTS

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SCIENTIFIC PAPER

UDC

Highlights

- Enhanced polyurethane degradation using DES and ultrasonication.
- Green solvent for polyurethane recycling
- Green recycling pathway for polyurethane waste
- Depolymerization of polyurethane to *o*-toluidine.

Abstract

This study explores the degradation of polyurethane (PU) using deep eutectic solvents (DES) combined with ultrasonic irradiation, aiming to develop sustainable recycling techniques for PU waste. DES, formed from choline chloride and urea, possesses environmentally friendly properties such as low toxicity and high solubility, making it suitable for chemical recycling. Degradation experiments were conducted at elevated temperatures (130-150 °C), both with and without ultrasonic assistance. The technique of GPC is applied to determine the molecular weight of raw PU and the degradation product. The structures of DES, PU, and its degradation products were analysed using FTIR and NMR. The results indicate that the application of ultrasonics significantly enhances the degradation rate at approximately 5.20% from 58.51 ± 0.04% to 63.71 ± 0.03% at a constant temperature of 150 °C. This improvement is attributed to cavitation-induced effects, which facilitate polymer chain breakdown. Molecular transformations were confirmed through the presence of NH_3 *groups resulting from the break of the PU structure to form o-toluidine, as identified by NMR. Reaction pathways were established through structural analysis of both raw PU and its degradation products. These findings demonstrate the potential of ultrasonic-assisted DES in advancing chemical recycling strategies for PU, addressing environmental concerns related to persistent PU waste, and promoting sustainable waste management practices.*

Keywords: Ultrasonic, Polymer recycling, o-toluidine.

INTRODUCTION

Polyurethane (PU) represents a multifaceted polymer extensively employed in diverse industrial applications, attributed to its remarkable characteristics such as durability, flexibility, and abrasion resistance [1]. PU is frequently utilized in a variety of applications, including foams, adhesives, coatings, elastomers, and membranes [2-5]. PU has also proven to be applied as a sheath for elastic electromagnetic fibers [6]. Its versatile properties have established it as a preferred material across multiple sectors, including construction, automotive, and consumer goods. The persistent nature of PU presents serious environmental problems, notwithstanding its benefits. Conventional disposal methods for non-biodegradable materials, including landfilling and incineration, are unsustainable [7]. These practices result in the accumulation of PU waste, which significantly contributes to environmental pollution.

Recent advancements have highlighted a growing focus on the formulation of sustainable recycling methodologies aimed at mitigating the environmental challenges posed by PU waste. Various techniques have been established for the degradation of PU, encompassing thermal, chemical, biological, and mechanical recycling methods. Chemical degradation is extensively researched due to its potential for recovering valuable raw materials

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such as polyols and amines. Common methods of chemical degradation encompass glycolysis, hydrolysis, aminolysis, and alcoholysis [8-10]. However, these techniques sometimes involve the use of hazardous solvents, high temperatures, or lengthy reaction times, which lessens their viability from an economic and environmental standpoint [9,11]. The innovations are not only focused on the PU recycling process but also on other sustainable strategies. They include innovations in sustainable plastics, such as a new biocompatible and biodegradable polyurethane elastomer with self-healing properties [12], recyclable and degradable gelatin glycerohydrogel [13]. Despite the various technically feasible methods of polyurethane recycling and sustainable products, the current recycling rate is below 10%, with the majority ending up in landfills [14].

The emergence of deep eutectic solvents (DES) as environmentally friendly solvents offers a novel approach to addressing the issues associated with polyurethane degradation. DES are synthesized through the interaction of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) at defined molar ratios, resulting in distinctive characteristics including low toxicity, elevated solubility, and diminished volatility [15-17]. The aforementioned characteristics significantly augment their applicability in chemical recycling processes.

Ultrasonic irradiation represents an advanced methodology that has garnered significant interest due to its capacity to accelerate degradation processes. Ultrasonic waves facilitate the generation of cavitation bubbles, which induce localized high temperatures and pressures, thereby markedly improving the degradation of polymer chains in the presence of DES [18]. A combination of DES and this method facilitates the recovery of valuable monomers while promoting a more environmentally sustainable approach to addressing polyurethane waste. Thermoplastic PU, which consists of o-toluidine and polycarbonate diol (PCDL), was utilized in this study.

Recent advancements in plastic waste management highlight the significance of integrating green chemistry principles into recycling technologies. Many studies have highlighted the necessity of sustainable degradation solutions that reduce environmental impact while facilitating the effective recovery of valuable monomers [19]. Current research conducted by Zhang *et al.* explores novel solvent systems, including DES and their role in enhancing the depolymerization of PU under milder reaction conditions [14]. The recent advancements highlight the importance of investigating environmentally sustainable and scalable methods, such as DES-assisted degradation, especially when integrated with physical enhancements like ultrasound to enhance degradation rates and optimize material recovery.

This study investigated the effect of ultrasonic irradiation at different temperatures on the PU degradation in the DES. Degradation of PU was investigated through the o-toluidine structure identification using 1H NMR spectra. The research aims to enhance sustainable waste management strategies for polyurethane materials, thereby advancing polymer recycling and addressing critical environmental issues.

EXPERIMENTAL

Materials

The high flow thermoplastic polyurethane (TPU) was obtained from Revlogi Materials Solutions Sdn Bhd (Malaysia). Urea and choline chloride (ChCl) were obtained from Sigma-Aldrich, Germany. Acetone was obtained from HMBG Chemical, Germany. The solvent used for NMR was deuterated dimethyl sulfoxide (DMSO-d_6) obtained from Sigma Aldrich, Germany.

Preparation of DES

ChCl and urea were mixed with a ratio of 1:2 at 70 ℃ for 2 h until a clear, transparent, and homogeneous mixing liquid was obtained.

Physical Properties of DES

Density

The pycnometer was used to determine the density of the DES components (ρ_L), which was calculated by Eq. (1) [20].

$$\rho_L = \frac{m_L}{m_{H2O}} \cdot \rho_{H2O} \tag{1}$$

where m_L is the mass of liquid, m_{H2O} is the mass of water, and ρ_{H2O} is the density of water. The measurement was conducted in duplicate.

The average absolute deviation (AAD) was calculated for each set of measurements by Eq. (2):

$$AAD = \frac{1}{N}\sum_{I=1}^{N} \frac{\left|x_i - \bar{x}\right|}{x_i} \tag{2}$$

where n is the number of runs for one experimental condition, N is the total number of runs, x_i is the data for one experimental condition and $\bar{x}$ is the average for one experimental condition.

Viscosity

The viscosity of the DES was assessed by a regular viscosity (RV) spindle viscometer (Brookfield, United Kingdom) through the rotation of a spindle that was submerged in the liquid medium. The viscosity values were computed directly through the application of conversion factors derived from the scale readings corresponding to the specific rotational speeds [21]. The measurement was conducted in duplicate.

Degradation of PU in DES with and without a sonication-aided system

In this experiment, 25 g of the DES solution and 2.5 g of the PU were mixed in a 100 ml beaker. Then, the degradation took place at 130, 140, and 150 °C for 2 hours. The sample was subjected to the post-treatment process.

An ultrasonic bath (Scientz, SB-5200DTD, Ningbo, China) was used to perform sonication at a frequency of 40 kHz and an ultrasonic input power of 250 W. The degrading process was conducted at 130, 140, and 150 °C for 2 hours. Then, the sample was prepared for the post-treatment process.

Post-treatment process after degradation of PU with and without a sonication-aided system

The degradation product was processed to separate the unreacted PU, DES, and the degradation product, namely o-toluidine. The mixture was cooled down to room temperature before being filtered with a 125 mm Whatman filter. The remaining unreacted PU made up the filter cake (1), while the DES and o-toluidine made up the majority of the filtrate (1).

Initially, an excess of distilled water was introduced into the filtrate (1) to separate o-toluidine (insoluble in water) and recover the DES (soluble in water) from the filtrate solution. This process was repeated once again to get filter cake (2) and filtrate (2). The filter cake (2) was then dried at 70 °C and measured as *W1*. The filtrate (2) was recycled using a vacuum rotary evaporator at 60 °C and 100 Pa to recover the DES.

The filter cake (1) was washed with distilled water to dissolve the remaining DES. This part of the DES was also recovered using the vacuum rotational evaporator at 60 °C. The clean filter cake (1) was completely dissolved in acetone to recover the unreacted PU. The filter cake (3) and filtrate (3) were obtained after the third filtering. The filtrate (3) mostly contained acetone and other possible degradation products, while the filter cake (3) contained the unreacted PU. A vacuum rotary evaporator was used to eliminate acetone from the filtrate (3) at 35 °C, and the unreacted PU was dried and measured as *W2*. The filter cake (3), which contained the unreacted PU, was then dried and weighed as *W3*. Figure 1 shows the overall process for the post-treatment process for the degradation of PU. Based on this posttreatment process, *W1* and *W3* were identified as o-toluidine and unreacted PU, respectively. The degradation rate was calculated by Eq. (3):

$$Degradation\,rate = \frac{W0 - W3}{W0} \cdot 100\% \qquad (2)$$

where *W0* is the initial weight of PU and *W3* is the weight of PU that was not degraded.

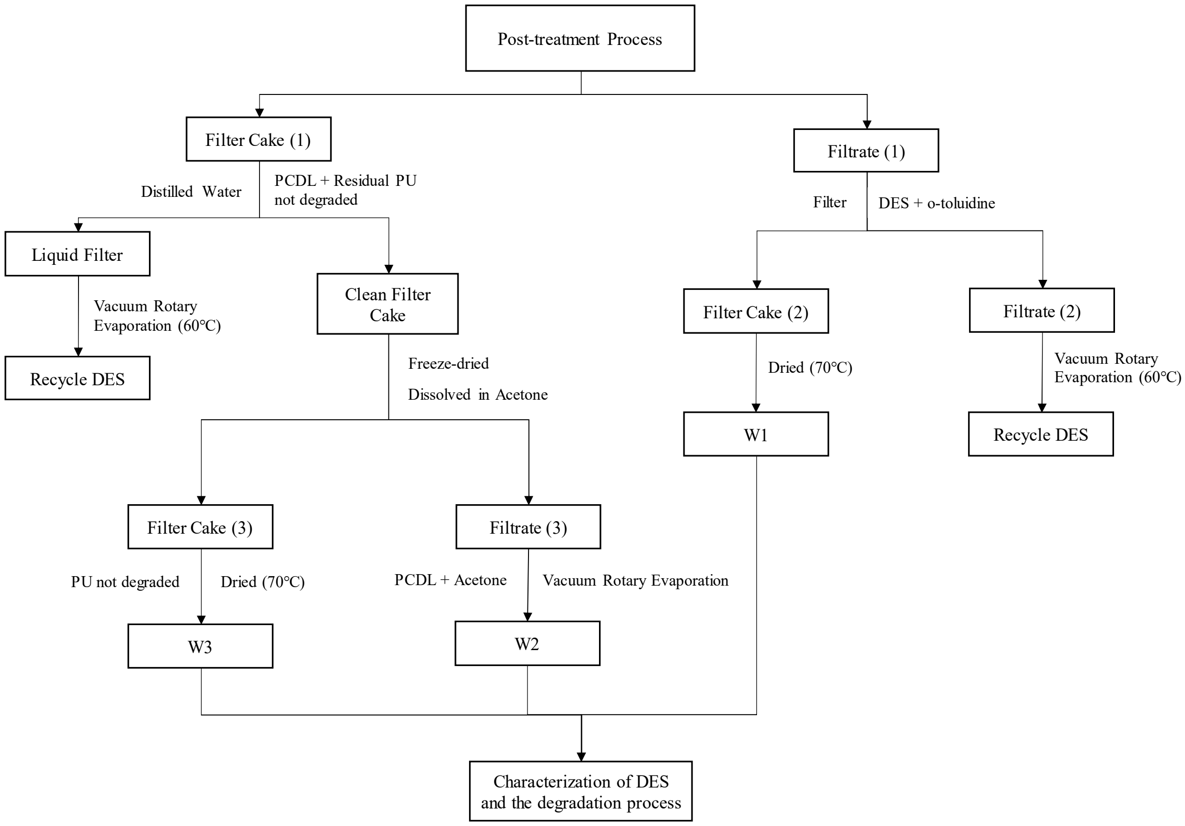

Figure 1. The overall post-treatment process for the degradation of PU.

Gel Permeation Chromatography

The molecular weight distribution of the raw polyurethane and the degradation products with and without sonication was analyzed using Gel Permeation Chromatography (GPC) (Agilent 1260 Infinity II LC, CA, USA). Tetrahydrofuran (THF) was used as the eluent at a concentration of 1.0 g/L and a constant flow rate of 0.6mL/min. The sample solution was prepared at a concentration of 1.0 g/L, and an injection volume of 50.0 µL was used for each run with a flow rate of 0.6 mL/min. Detection was carried out using a refractive index detector (RID1A, Refractive Index Signal). The delay volume was set to 0.0 mL, and data acquisition was performed at an interval of 0.21 seconds.

Characterization of DES and the degradation product

FT-IR spectra of the DES solvent and its degradation products were obtained using a Perkin-Elmer (USA) spectrometer within the wave-number range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}.

To study the structure of degradation products, 1H NMR spectra were recorded using an AVANCE 3TM spectrometer (Bruker, Switzerland) operating at a frequency of 400 MHz. The solvent employed for NMR analysis was deuterated dimethyl sulfoxide (DMSO-d_6).

RESULTS AND DISCUSSION

Physical Properties of DES

Key physical properties of the DES as an efficient solvent are viscosity and density. Table 1 shows the physical properties of ChCl and urea in comparison with the previous study.

The measured density of the synthesized DES was determined to be 1.19 ± 0.01 g/cm³, which was comparable with the literature value of 1.24 g/mL [18]. ChCl acts as a hydrogen bond acceptor, whereas urea acts as a hydrogen bond donor. The high density of this DES arises from the strong hydrogen-bonding interactions between ChCl and urea, leading to a tight molecular structure [22,23]. These interactions decrease intermolecular distances, resulting in a compact and cohesive solvent structure. The strong hydrogen-bonding environment of the ChCl-urea DES boosts its efficacy in polymer solubilization [14]. The density of the DES aligns closely with literature values for comparable DES formulations, thereby confirming the reliability of this property in promoting degradation reactions.

The synthesized DES had a viscosity of 755 ± 0.14 cP, comparable with the literature value of 750 cP [17]. Viscosity is another key physical parameter that impacts polymer degradation in solvent systems. The solvent's viscosity affects its flow and interaction rate with polyurethanes. The viscosity found is noticeably altered by a strong hydrogen-bonding network between ChCl, an ionic chemical, and urea, a polar molecule [24]. These component interactions raise viscosity by increasing internal friction [25]. ChCl ionic properties improve viscosity by slowing solvent molecules and generating a structured fluid network. ChCl and urea mixed at this ratio provide a viscosity greater than expected from their separate components, indicating strong intermolecular interactions. Lower viscosity usually allows for greater mixing and quicker solute diffusion, which may greatly speed up chemical processes in the solvent.

Table 1. Properties of the DES.

Properties	This work	Literature Review	Ref.
Density, ρ (g cm^{-3})	1.19 ± 0.01	1.24	[15]
Viscosity, $\mu\,(cP)$	755 ± 0.14	750	[41]

Characterization of the DES and degradation products

The Fourier Transform Infrared (FTIR) spectra were recorded to identify significant functional groups present in the DES obtained from ChCl and urea are shown in Figure 2(a). The vibrational bands observed at 3329 cm^{-1} correspond to the symmetric stretching mode of the amide functional group (-NH) present in urea [26]. The vibrational band observed at 3203 cm^{-1} is attributed to the O-H stretching modes associated with hydroxyl groups present in ChCl. This observation suggests the presence of a robust hydrogen bonding interaction between the constituent components. The peaks rarely visible at 3000 cm^{-1} were attributed to the CH stretching vibrations of alkyl groups present in ChCl, indicating its role in the structural integrity of the solvent [27]. Additionally, the peak at 958 cm^{-1} is associated with C-N stretching vibrations linked to the quaternary ammonium group of ChCl, reflecting the ionic characteristics of the deep eutectic solvent. The observed peaks at 1670 cm^{-1} and 1618 cm^{-1} are attributed to the urea functional group [27]. The spectral bands observed at 1670 cm^{-1} are indicative of C=O stretching associated with amide functional groups, while the band at 1618 cm^{-1} corresponds to N-H scissoring vibrations. The observed peaks validate the presence of carbonyl and amine groups in urea, which engage with ChCl to enhance the stability of the deep eutectic solvent structure.

PU is a high polymer characterized by a repetitive urethane bond (-NHCOO-), which is synthesized through the polymerization process involving isocyanates and polyols. Figure 2(b) shows the FTIR spectrum of PU. A prominent peak observed at 3350 cm^{-1} corresponds to N-H stretching. The observed peak at 1732 cm^{-1} was attributed to the ester C=O. The additional peak observed at 1602 cm^{-1} corresponds to C=C vibrations within benzene rings. Soft segment polyether polyols exhibit the C-H stretching vibration at 2967 cm^{-1} [28,29].

Degradation product

The influence of temperature on the degradation rates of PU was examined under two different conditions: without sonication and with sonocatalytic assistance. Four distinct temperatures, 130, 140, 150, and 160 ℃, were utilized, and the experiments were conducted for two hours. Figure 3 shows the effect of the temperature on the degradation of PU.

Without sonication, the degradation rate of PU was measured at 27.41 ± 0.02% at 130 °C. When the temperature increased to 140 °C, the degradation rate more than doubled, reaching 52.12 ± 0.07%. Further elevation to 150°C resulted in a degradation rate of 58.51 ± 0.04%. This shows that longer reaction time and higher temperature are important to achieve complete breakdown of the polymer. These findings suggest that thermal conditions significantly influence the polymer breakdown, as higher temperatures enhance molecular kinetic energy, increasing the probability of chemical bond disruption [30]. The urethane linkages, which are the characteristic backbone of PU, become more susceptible to cleavage as the provided energy surpasses the activation threshold necessary for bond rupture [31]. Moreover, increased temperatures improve the interaction between the DES and the PU matrix, enhancing solvent solubility and diffusion. This process facilitates deeper penetration, which promotes chemical structure breakdown, primarily targeting urethane and urea bonds crucial for polymer stability [10].

Under sonication-assisted degradation, the degradation rates were significantly higher. At 130 °C, the degradation rate reached a 19.79 ± 1.75% decrease in

7.62% compared with the process without sonication assistance. When the temperature increased to 140 °C, the degradation rate rose to 54.79 ± 0.02% and at 150 °C, it further escalated to 63.71 ± 0.03%. A clear improvement in plastic degradation was also observed in the study by Attallah *et al.* [32]. In this research, the biodepolymerization of PET showed an increase of around 16% (w/w) in monomer conversion when sonication was applied together with enzymatic treatment, compared to the process without using sonication [32]. This method can be useful for improving the biodegradation process of plastics in more eco-friendly conditions.

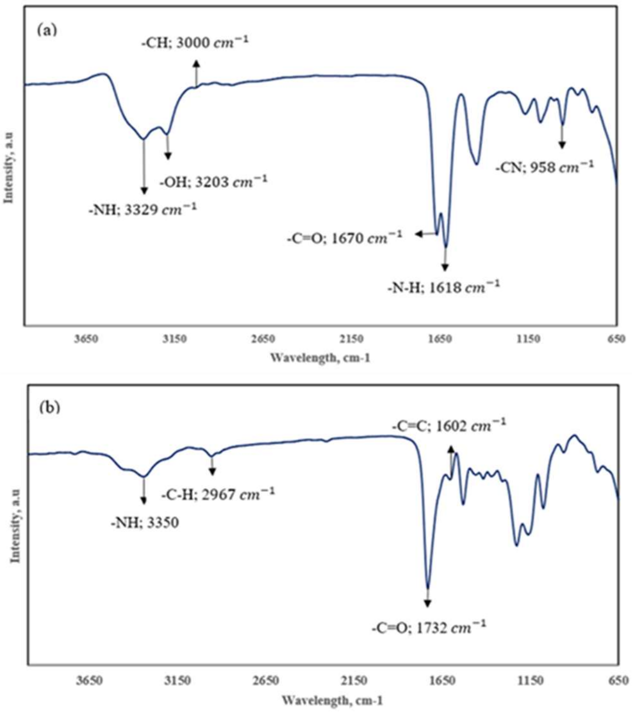

Figure 2. The FTIR spectra: a) DES and b) PU.

The higher efficiency observed in sonication-aided degradation can be attributed to the combined effects of ultrasonic irradiation and elevated thermal conditions. The key mechanism contributing to this enhancement is cavitation, where rapid formation and implosion of microbubbles generate localized hot spots with extreme temperature and pressure [18,33,34]. These localized conditions intensify the degradation process by accelerating polymer bond rupture beyond what is achievable with thermal degradation alone.

Additionally, ultrasonic waves decrease solvent viscosity, which further optimizes mass transfer characteristics [31]. A solvent with lower viscosity allows for better penetration and interaction between DES and the PU matrix, improving solvation and degradation. This enhanced mass transfer ensures a uniform distribution of reactants, leading to more efficient degradation. Furthermore, ultrasonic waves intensify molecular motion, promoting more successful collisions between reactant molecules. These amplified interactions facilitate essential chemical reactions, accelerating the cleavage of weaker bonds and leading to the generation of smaller molecular fragments that are more prone to further degradation [35].

Overall, the results demonstrate that both thermal conditions and ultrasonic assistance play crucial roles in polyurethane degradation. The increase in kinetic energy at elevated temperatures enhances polymer bond disruption and solvent interactions, leading to higher degradation rates. In conclusion, the presence of ultrasonic irradiation significantly amplifies these effects through cavitation, enhanced mass transfer, and increased reaction rates. The synergistic combination of temperature and ultrasonic assistance presents a promising approach to optimizing PU degradation, offering insights into improved recycling methodologies for PU waste.

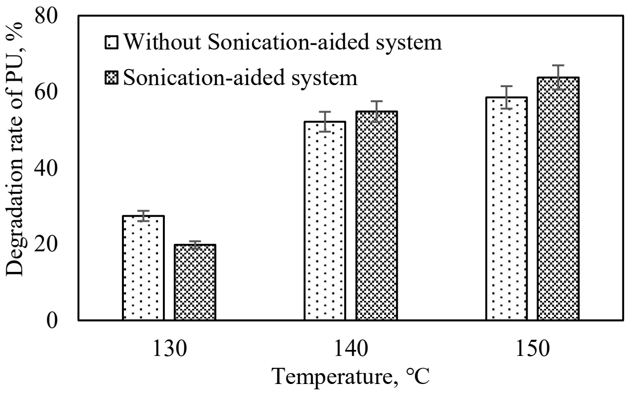

Figure 3. Effect of temperature on the degradation of PU in the DES.

Characterization of the Degradation product

Figure 4 shows the functional groups identified in the *W3*, consisting of the unreacted PU facilitated with and without a sonication effect.

The analysis reveals multiple peaks, with significant peaks identified at 3424 cm^{-1} and 3327 cm^{-1} were attributed to the amine (-NH) groups. The peaks observed at 1676 cm^{-1}, 1699 and 1732 cm^{-1} correspond to the presence of C=O functional groups, while the peaks at 1089 cm^{-1} and 1084 cm^{-1} are associated with the C-O group [36]. Furthermore, the observed peaks at 769 cm^{-1} indicate the presence of C-H functional groups. The results indicate that the functional groups present in the original PU have transformed into new groups within the residual material, thereby demonstrating the effective degradation of urethane bonds throughout the degradation process. The transformation resulted in the generation of smaller molecular entities, such as alcohols, ethers, and carboxylic acids, while retaining certain aromatic compounds [37]. The sonication-assisted degradation process effectively modifies the molecular structure of PU by the existence of a new group at 1236 cm^{-1}.

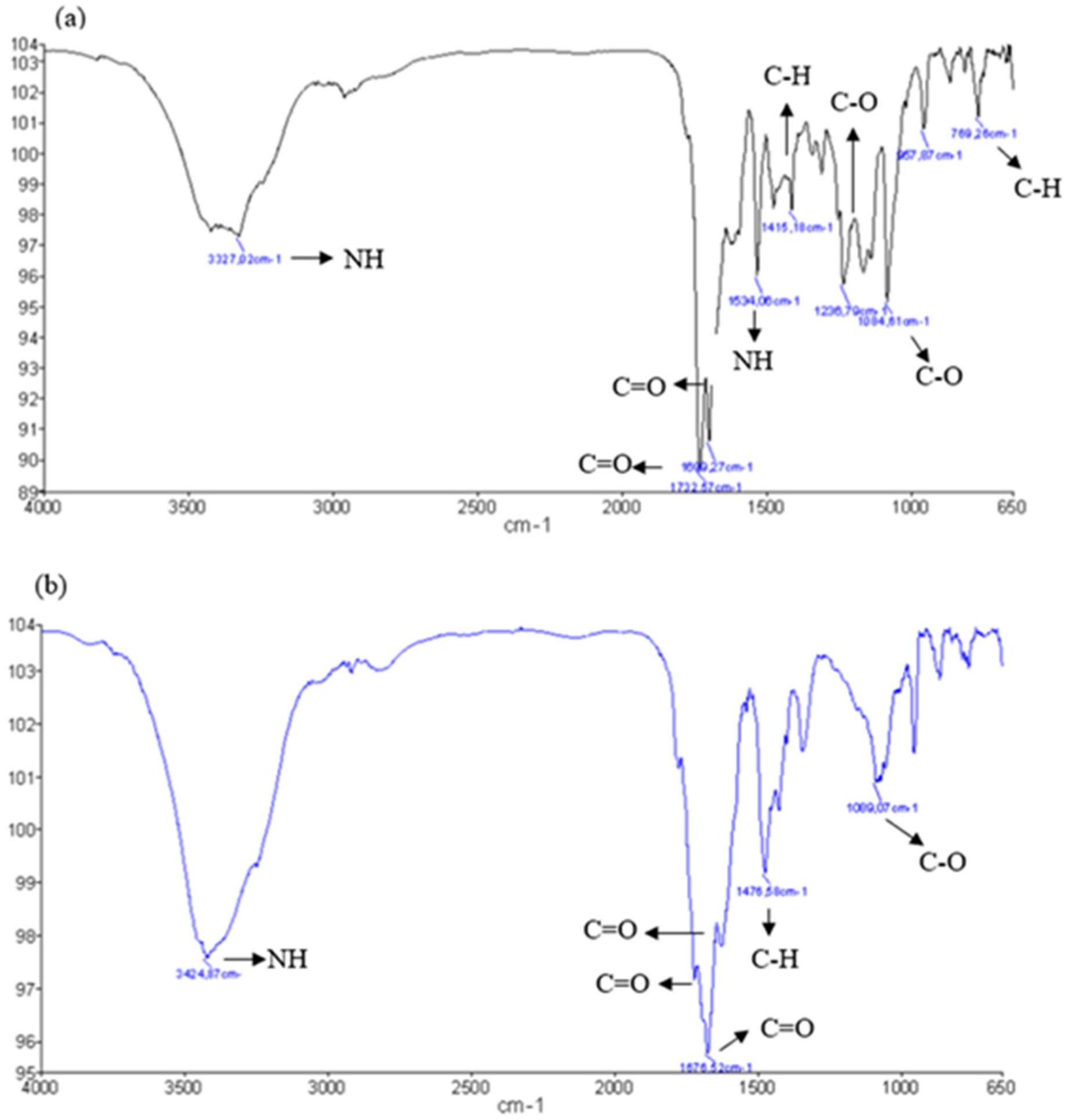

Figure 4. FTIR analysis of the unreacted PU (W3) (a) without and (b) with sonication.

Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) was used to determine the molecular weight distribution of the raw PU before the degradation process. The chromatogram presented in Figure 5 displays a clear monomodal distribution, suggesting a consistent molecular weight distribution throughout the sample. The primary elution peak is observed at an elution volume ranging from 6.5 to 7.5 mL, which is indicative of high molecular weight polymer fractions. The number average molecular weight (*Mn*) was determined to be 5.985×10^3 g/mol, while the weight average molecular weight (*Mw*) was found to be 9.080×10^4 g/mol, resulting in a polydispersity index of approximately 15.17. The observed high PDI indicates a wide molecular weight distribution, which is characteristic of PU produced through step-growth polymerization processes, where the regulation of chain length is not as precise as in living polymerization methods [38]. The tailing observed at elevated elution volumes 9 to 11 mL suggests the presence of lower molecular weight species or oligomers, which may include residual monomers or partially polymerized chains [38,39].

Figure 5 displays the GPC chromatogram of the degradation product, *W1*, which was derived from the degradation of PU in DES without the aid of sonication. The chromatographic profile indicates a narrower distribution of lower molecular weight species when compared to the raw polyurethane and the sonication-assisted degradation. The main peak is observed at an elution volume ranging from 8.5 to 9.5 mL, indicating the presence of smaller polymer fragments or monomeric degradation products. The *Mn* was determined to be 2.74×10^2 g/mol, while the *Mw* was measured at 6.47×10^2 g/mol, leading to a PDI of 2.36. This suggests a moderate degree of polymer chain scission and a more uniform distribution of molecular weight in comparison to the original polyurethane, with a value of 15.17. The chromatogram displays a distinct single peak, accompanied by minimal signals at low elution volumes, indicating a restricted degradation into very low molecular weight compounds or oligomers [40]. The transition from the original high molecular weight region validates the occurrence of degradation. The tailing observed at elevated elution volumes 9 to 11 mL suggests the presence of lower molecular weight species or oligomers, which may include residual monomers or partially polymerized chains.

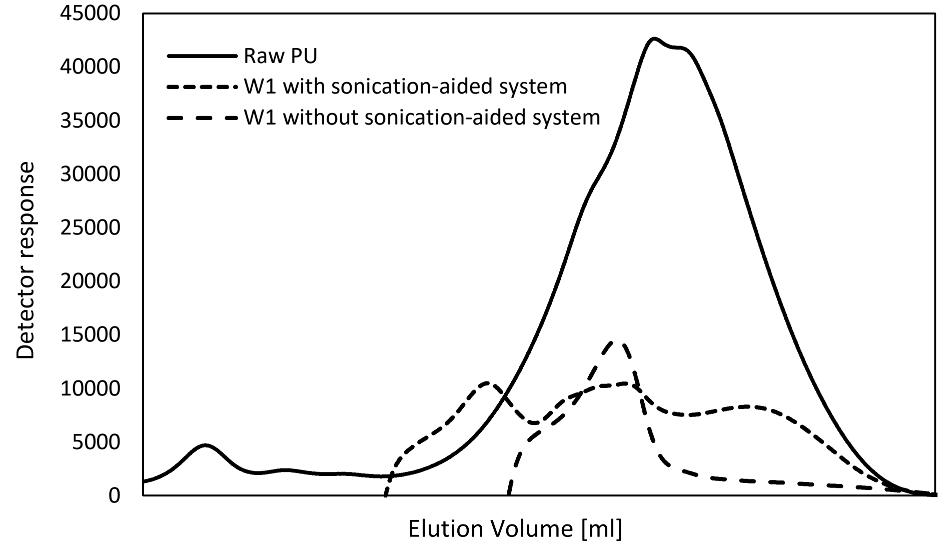

Figure 5. GPC traces recorded with the RID1A: a) raw PU, b) W1 without the sonication-aided system, and c) W1 with the sonication-aided system.

Table 2. GPC data for the molecular determination.

Sample	Raw PU	*W1* without the sonication-aided system	*W1* with the sonication-aided system
Number average molecular weight, *Mn* (g/mol)	5.99×10^3	2.74×10^2	6.29×10^2
Weight average molecular weight, *Mw* (g/mol)	9.08×10^4	6.47×10^2	3.37×10^3
Z-average molecular weight, *Mz* (g/mol)	2.13×10^5	2.83×10^3	1.03×10^4
Polydispersity index, PDI	15.17	2.36	5.36

W1 is identified as o-toluidine calcuted using posttreatment method described in Figure 1.

The chromatogram of *W1* with a sonication-aided system exhibits a notable shift toward elevated elution volumes in comparison to raw polyurethane, signifying a considerable decrease in molecular weight. The *Mn* of the *W1* product was determined to be 6.29×10^2 g/mol, while the *Mw* was found to be 3.37×10^3 g/mol, leading to a calculated PDI of 5.36. This indicates a significant reduction from the initial *Mn* and *Mw* values of 5.98×10^3 g/mol and 9.08×10^4 g/mol, respectively. The observed lower molecular weights and narrower peak profiles indicate significant depolymerization of the polyurethane backbone, thereby demonstrating the effectiveness of sonication-assisted DES treatment in the breakdown of polymer chains. The chromatographic profile displays multiple distinct peaks within the range of 7.8 to 9.5 mL, which are associated with lower molecular weight degradation products. The lack of a notable peak in the lower elution volume range 6 to 7 mL, where the high molecular weight polymer was previously identified, reinforces the successful degradation of the original polymer structure. The detection of o-toluidine, an aromatic amine that arises from the degradation of urethane linkages, aligns with earlier findings regarding the depolymerization of polyurethane. The reduction in molecular weight due to sonication demonstrates the combined effects of cavitation and localized high-energy zones in improving DES-based depolymerization [41].

Chemical structure analysis using 1H NMR

The structure of the degradation product was analyzed using NMR analysis to provide valuable insights into the chemical composition and structure during the process. Figure 6 shows the 1H NMR spectra.

The peaks at 5.5 ppm were assigned to the NH_2 group, while the peaks at 2.0-2.1 ppm were assigned to the CH_3 group. PU found that the chemical shifts of the groups are 8.3 ppm (NH), 5.9-6.7 ppm (aromatic), 2.2-2.6 ppm (CH), 1.1 ppm (CH_3) [29]. The degradation of PU using a DES formulated from ChCl and urea was examined to assess its efficacy in breaking the polymer structure. Figure 7 illustrates the breakage of urethane (-NH-COO-) connections, resulting in the generation of lower molecular weight fragments known as o-toluidine and PCDL.

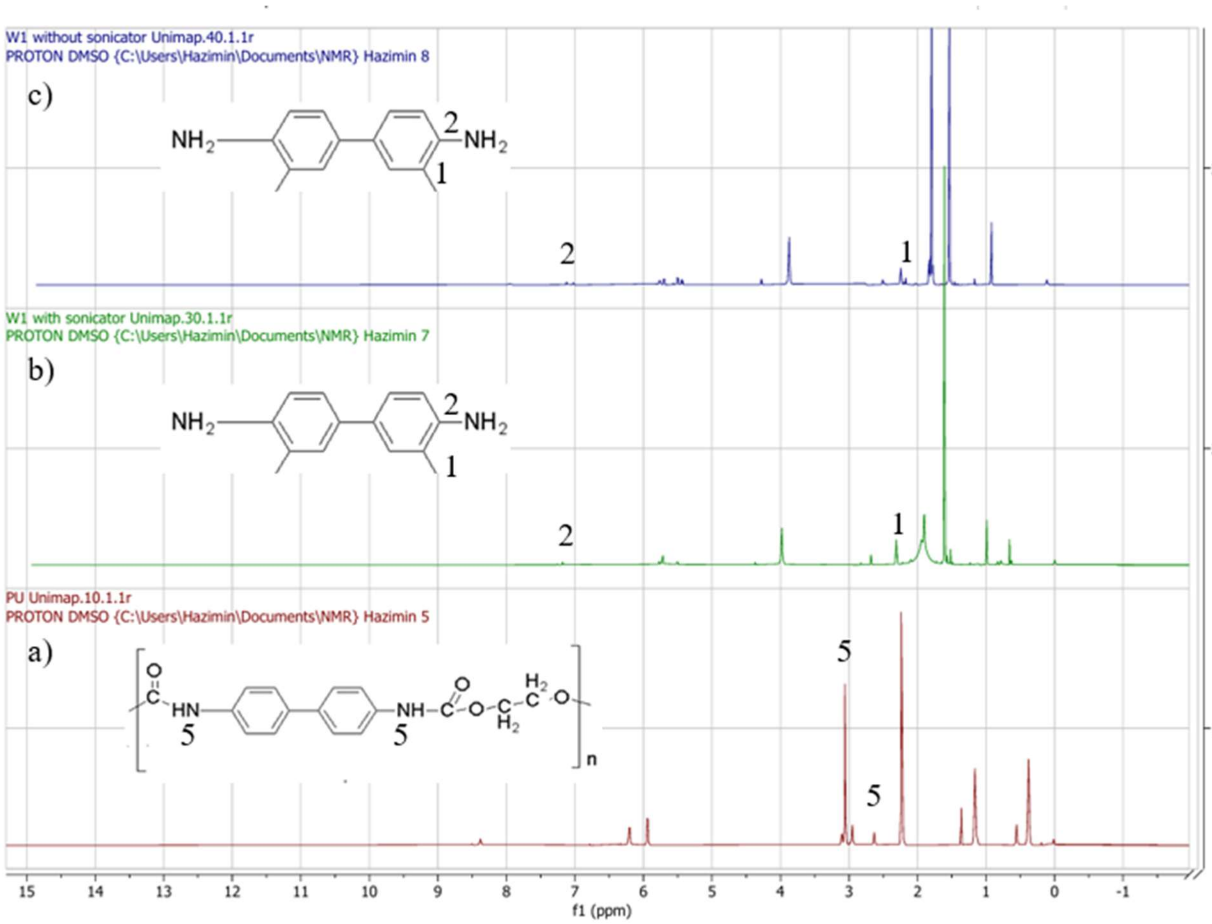

Figure 6. The 1H NMR spectrum of the W1: a) raw PU, b) W1 in the sonication-aided system, and c) W1 without the sonication-aided system. The solvent used for NMR was DMSO-d_6.

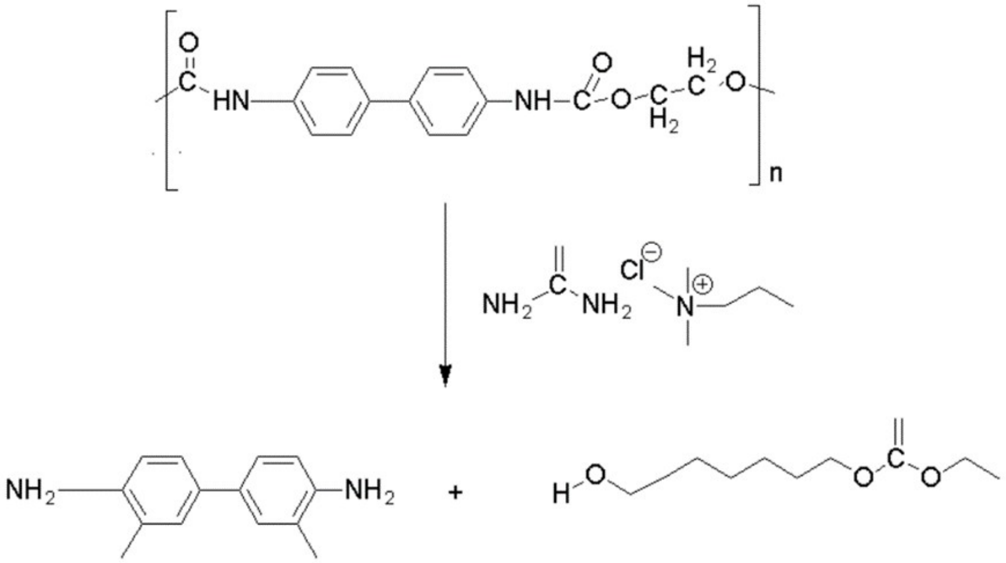

Figure 7. The degradation route of the PU elastomer.

In this study, the *W1* or o-toluidine structure was used for the structure identification after the degradation process, as shown in Figure 7. The DES medium promotes polyurethane breakdown via nucleophilic assault and hydrogen bonding interactions. The chloride anion in ChCl, in conjunction with urea, establishes strong hydrogen bonds with the carbonyl groups of urethane links, enhancing their vulnerability to nucleophilic cleavage [42]. The existence of protonated amines ($-NH_3^+$) in the degradation products indicates that the process occurs via a partial hydrolysis mechanism, whereby urea facilitates the breaking of urethane bonds. The release of an aromatic diamine fragment signifies the degradation of the hard segment of polyurethane. This indicates that the degradation process efficiently severs the bonds linking the diisocyanate-derived segments of the polymer. The existence of polyol degradation products with hydroxyl (-OH) and carbonate (-COO-) functionalities indicates that the soft section of PU also experiences cleavage. The identified structures suggest hydrolysis or aminolysis of ester and carbonate moieties within the polymer backbone.

DESs provide an environmentally friendly option for the solubilization and depolymerization of polyurethane, owing to their capacity to dissolve and engage with polymeric structures. ChCl and urea create a eutectic combination characterized by robust hydrogen bond donor-acceptor interactions that enhance the degradation process [43]. In contrast to traditional aggressive chemical treatments, DES-based degradation provides a more eco-friendly method with less toxicity. The capacity of DES to decompose PU into its precursor constituents indicates prospective uses in polyurethane recycling and waste management. The extraction of diamines and polyols from polyurethane degradation facilitates their reutilization in polymer synthesis, hence reducing the need for fresh raw materials. Moreover, the moderate reaction conditions of DES-based degradation reduce the generation of toxic by-products, making it a sustainable choice for plastic waste processing.

CONCLUSION

This research effectively illustrates the potential benefits of deep eutectic solvents (DES) combined with ultrasonic irradiation in enhancing polyurethane (PU) degradation. The results indicate a remarkable increase in degradation efficiency, with rates rising from 19.79 ± 1.75% at 130 °C to 63.71 ± 0.03% at 150 °C under ultrasonic assistance. In contrast, degradation rates without sonication only reached a maximum of 27.41 ± 0.02% to 58.51 ± 0.04% under similar temperature conditions. The breakdown of PU polymer chains is greatly accelerated by the application of ultrasonic vibrations, which promote the formation of cavitation bubbles and localized areas of high temperature and pressure. This process marks a substantial improvement in chemical recycling techniques, especially when combined with the beneficial properties of DES, such as their high solubility for PU and low toxicity. PU degradation but also provided insight into ways to recycle polyurethane waste into valuable products. Overall, this research highlights the synergistic benefits of employing DES and ultrasonic irradiation, presenting a promising strategy for addressing the environmental issues caused by persistent PU waste while paving the way for more sustainable waste management practices. Future studies may explore the higher temperature and longer reaction time to achieve the maximum degradation rate.

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POTENCIJAL ULTRAZVUČNOG ZRAČENJA U RAZGRADNJI POLIURETANA U EUTEKTIČKIM RASTVARAČIMA

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NAUČNI RAD

Ovaj rad istražuje razgradnju poliuretana (PU) korišćenjem eutektičkih rastvarača (DES) u kombinaciji sa ultrazvučnim zračenjem, sa ciljem razvoja održivih metoda reciklaže PU otpada. DES, dobijen od holin hlorida i uree, poseduje ekološki prihvatljiva svojstva, kao što su niska toksičnost i visoka rastvorljivost, što ga čini pogodnim za hemijsku reciklažu. Eksperimenti razgradnje su sprovedeni na povišenim temperaturama (130-150 °C), sa i bez efekta ultrazvuka. Molekulske mase sirovog PU i proizvoda razgradnje određene su gel permeacionom hromatagorafijom. Strukture DES, PU i proizvoda razgradnje su analizirane korišćenjem FTIR i NMR. Rezultati pokazuju da primena ultrazvuka značajno povećava stopu razgradnje za približno 5,20% (od 58,5% do 63,7%) na konstantnoj temperaturi od 150 °C. Ovo poboljšanje se pripisuje efektima izazvanim kavitacijom, koji olakšavaju raskid polimernog lanca. Molekularne transformacije su potvrđene prisustvom NH_3 *grupa koje nastaju usled raskida strukture PU da bi se formirao o-toluidin, što je identifikovano NMR spektroskopijom. Reakcioni putevi su utvrđeni strukturnom analizom i sirovog PU i proizvoda njegove razgradnje. Ovi nalazi pokazuju potencijal DES uz dejstvo ultrazvuka u unapređenju strategija hemijske reciklaže PU, rešavanju ekoloških problema vezanih za postojani PU otpad i promociji održivih praksi upravljanja otpadom.*

Ključne reči: Sonohemija, Reciklaža polimera, o-toluidin.