16th International Fiber and Polymer Research Symposium (16th ULPAS)
9-10 May, 2025, Istanbul technical University (ITU), Istanbul, Türkiye

Amphiphilic Functional Polymers as Polypropylene Nonwoven Surface Treatment

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ABSTRACT

Polypropylene nonwovens (PP NWs) are utilized commonly in baby diapers, adult incontinence products, feminine hygiene items, and wet wipes. Due to the inherent hydrophobic character of these NWs, their properties are significantly influenced by hydrophilic surface treatments to enhance both their performance and the user experience. Although polymer-based formulations offer great versatility, small molecule applications are more prominent in industry. This study proposes an amphiphilic functional polymer-based surface treatment for NW disposable hygiene products. Such polymer offers odor control, enzymatic inhibition, pH control, controlled release of active agents, and antimicrobial activity. This article discusses the synthesis of the as-utilized polymer, succinylated Poly(2-propyl-2-oxazoline-co-ethyleneimine) (S-PPrOZ-PEI), and its characterization by both Fourier-Transform Infrared Spectroscopy (FTIR) and Nuclear magnetic resonance (NMR). Additionally, the preparation of a dilute polymer-based aqueous formulation, and its utilization as a surface treatment to PP NWs are described here. S-PPrOZ-PEI modifies the PP NW surface through its hydrophobic interactions with PP and makes the surface more hydrophilic due to the presence of acid functional groups in its structure. The performance of the applied formulation is evaluated through contact angle measurements, and then they are compared to commercial small-molecule-based surface treatment formulations, which are found to be similar.

Keywords: Nonwoven Surface Treatments, Amphiphilic Polymers, Hydrophilicity, Contact Angle

I. INTRODUCTION

Poly(2-alkyl-2-oxazoline)s (POZ) have garnered significant attention in recent years due to their tunable physicochemical properties, biocompatibility, and potential for post-polymerization modifications. Among them, poly(2-propyl-2-oxazoline) (PPrOZ) is of particular interest owing to its slightly hydrophobic nature, and capability to be modified to obtain amphiphilic structures, which makes it a promising candidate for surface modification as well as biomedical applications. However, its inherently limited hydrophilicity poses a challenge for applications where enhanced wettability, and aqueous compatibility are desired.

Surface hydrophilization of polymeric substrates, especially NW materials composed of PP, is critical in various fields, including filtration, medical textiles, and personal care products. These materials are naturally hydrophobic, which limits their ability to interact with the aqueous media. As a result, considerable research efforts have focused on developing effective surface functionalization strategies to modulate their wettability [1].

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In this study, a multi-step chemical approach to enhance the hydrophilic properties of PP NW substrates through tailored polymer coatings is reported. Initially, a PPrOZ homopolymer was synthesized through a cationic ring-opening polymerization (CROP), and then it was subsequently hydrolyzed to obtain a copolymer with poly(ethyleneimine) (PEI) segments. The as-hydrolyzed copolymer was then subjected to succinylation, which introduced pendant carboxylic acid groups, and yielded the S-PPrOZ-PEI derivative. The as-modified polymers were characterized by both ^{1}H NMR and FTIR spectroscopy to confirm successful structural transformations at each stage.

To assess the surface performance of these polymers, contact angle measurements were conducted on PP NW substrates treated with PPrOZ, S-PPrOZ-PEI, and two different commercial benchmark formulations. By analyzing the dynamic behavior of water droplets on the as-treated surfaces, the influence of each formulation on the NW materials' surface was evaluated.

This work aims to contribute to the development of next-generation surface functionalization methods by using tailored polyoxazoline-based polymers, offering a sustainable and efficient alternative to conventional hydrophilic coatings for polymeric substrates.

II. EXPERIMENTAL METHOD

2.1 Synthesis of PPrOZ Homopolymer

The synthesis of PPrOZ homopolymer was carried out following the previously established methodologies by the current research group [2,3]. Briefly, the monomer (2-propyl-2-oxazoline) and chlorobenzene were added into a N_2-purged, oven-dried round-bottom flask. The monomer concentration of the monomer was adjusted to 4M. Here, trifluoromethanesulfonic acid (TfOH) was employed as the initiator, and a monomer-to-initiator ratio ([M]/[I]) of 50 was maintained to achieve a targeted molecular weight of approximately 5,000 g/mol. The polymerization was quenched by the addition of a methanolic potassium hydroxide (KOH) solution. After the termination of the polymerization, solvents were removed under reduced pressure. The residual solids were dissolved in dichloromethane (DCM) and then filtered. The organic phase was dried by using sodium sulfate (Na_2SO_4) and filtered. Following the DCM's evaporation, the polymer was redissolved in methanol, and then it subsequently precipitated in cold diethyl ether ($(C_2H_5)_2O$).

2.2 Hydrolysis of PPrOZ Homopolymer

Hydrolysis of the PPrOZ homopolymer was performed in accordance with current group's earlier kinetic studies, and protocols[1]. The homopolymer was weighed and dissolved in 4 M HCl solution in a two-neck flask. The reaction was proceeded at 100 °C for 52 minutes to reach approximately 25% hydrolysis level. Following the reaction, the aqueous phase was washed once with diethyl ether, and then, neutralized with sodium hydroxide (NaOH) until the pH exceeded 10. Water was removed via evaporation, and the remaining material was first dissolved in ethanol, and then filtered, and subjected to further solvent removal under reduced pressure. The residual solids were redispersed in acetonitrile and maintained at 50 °C. The resulting mixture was filtered by using a Büchner funnel, and the organic layer was collected. After evaporating the solvent under vacuum, the PPrOZ-PEI copolymer was successfully isolated.

2.3 Succinylation of PPrOZ-PEI Copolymer

Succinylation of the PPrOZ-PEI copolymer was conducted in acetonitrile as the reaction medium. Initially, 4.16 g (0.9 mmol, 1 equivalent) of the copolymer was placed into a dry round-bottom flask, followed by the addition of 44 mL acetonitrile. The residual moisture was removed through azeotropic distillation, and 25 mL of the solvent was evaporated under vacuum. Succinic anhydride (1.17 g, 10 mmol, 12.60 equivalents) and triethylamine (3.25 g, 30 mmol, 36 equivalents) were then introduced. The mixture was refluxed under N_2 atmosphere at 80 °C for 24 h. Upon reaction completion, excess triethylamine and the solvent were removed under reduced pressure. The resulting solids were dissolved in 15 mL methanol, and then they precipitated into 250 mL of cold diethyl ether. After filtration, the polymer was redissolved in 40 mL of alkaline water (pH > 10) and extracted with 150 mL of diethyl ether. The aqueous layer was collected, acidified down to pH 2, and the remaining water was removed under vacuum. The final product was dissolved in 45 mL ethanol, filtered to remove NaCl, and the ethanol was evaporated to yield 4.8 g of S-PPrOZ-PEI as a light brown solid (Yield: 89%).

2.4 Characterization of Polymers

To verify the structures of the as-synthesized PPrOZ, PPrOZ-PEI, and S-PPrOZ-PEI polymers, proton nuclear magnetic resonance (^1H NMR) spectroscopy was carried out on 500 MHz Varian spectrometer by using $CDCl_3$ and CD_3OD as solvents. Also, the FTIR spectra were collected on a ThermoScientific Nicolet iS50 instrument equipped with an attenuated total reflectance (ATR) accessory.

2.5 Contact Angle Measurements

The performance of the formulations was assessed by contact angle measurements. In this method, a water droplet is placed on as-prepared PP NW samples, and its behavior is monitored over time. The droplet's movement is recorded by using a high-resolution camera, and the contact angle values at specific time intervals are determined through a dedicated image analysis software.

III. RESULTS AND DISCUSSIONS

The synthesis of PPrOZ homopolymer via CROP yielded a sample with well-defined spectral characteristics that are consistent with the previous reports about POZ systems.

In the ^1H NMR spectrum of the PPrOZ homopolymer, the signal appeared in the range of δ_a = 3.80–3.28 ppm (4H), corresponds to the methylene protons of the $-CH_2–CH_2–N-$ segments in the polymer backbone. Additionally, the propyl side chain protons were identified at δ_c = 2.22–2.47 ppm (2H, $-CH_2$), δ_d = 1.50–1.71 ppm (2H, $-CH_2$), and δ_e = 0.85–1.05 ppm (3H, $-CH_3$), as respectively shown in **Figure 1**.

Following the hydrolysis process, a new signal in the range of δ_b = 3.00–2.65 ppm (4H) was observed and was assigned to the $-NH–CH_2–CH_2-$ polymer backbone protons of the resulting ethyleneimine units. The hydrolysis degree was calculated in accordance with a previous study[1], by using the PPrOZ-PEI sample showing a hydrolysis rate of 23% after 52 minutes of reaction. Upon subsequent modification with succinyl anhydride, the peak attributed to the ethyleneimine units disappeared, and it had replaced by a new peak at δ = 2.35–2.60 ppm, corresponding to the methylene protons on the carboxylic acid side chains, confirming the successful succinylation.

Complementary FTIR analyses of PPrOZ 5K, PPrOZ-PEI, and S-PPrOZ-PEI are presented in **Figure 2.** All polymers exhibited characteristic CH_3 and CH_2 stretching vibrations at 2873–2961 cm^{-1} region, along with polyamide carbonyl (C=O) bands at 1626 cm^{-1}. In the FTIR spectrum of PPrOZ-PEI, a peak appeared at 3296 cm^{-1}, corresponding to the $-NH$ stretching vibration of the ethyleneimine units, which was absent in the PPrOZ 5K homopolymer. Additionally, the band at 1135 cm⁻¹, attributed to C–N stretching of secondary amines, further supported the presence of hydrolyzed units. As for S-PPrOZ-PEI, a distinct C=O stretching vibration was observed at 1728 cm⁻¹, confirming the presence of carboxylic acid groups. The complete disappearance of the −NH stretch in the modified polymer further indicated the successful and complete conversion during the succinylation step.

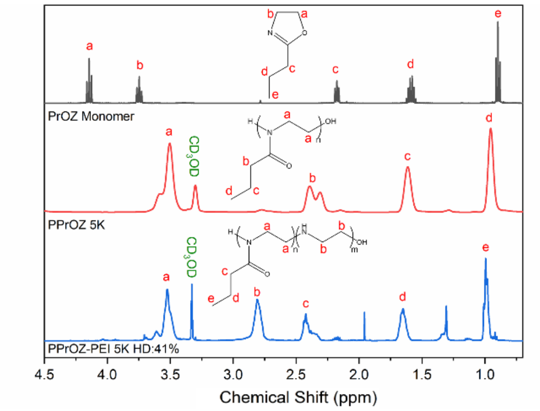

Figure 1. ^{1}H NMR spectra of PPrOZ, PPrOZ-PEI, and S-PPrOZ-PEI polymers.

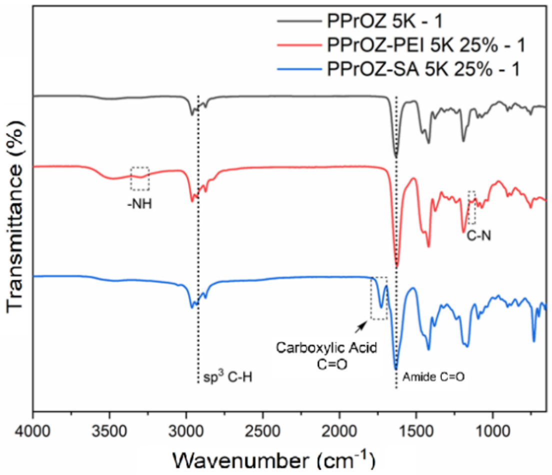

Figure 2. FTIR spectra of PPrOZ, PPrOZ-PEI, and S-PPrOZ-PEI polymers.

Here, the contact angle measurements revealed that the untreated NW samples exhibited a highly hydrophobic character, as expected (**Table 1**). The application of the PPrOz-based formulation resulted in a moderate decrease in contact angle values; however, it did not reach the level of hydrophilicity observed in commercial formulations. In contrast, the S-PPrOZ-PEI formulation demonstrated a notable enhancement in surface hydrophilicity. The comparative analysis of both initial (t = 0 s) and later (t = 3 s) time points further emphasized the superior wetting performance of the commercial formulations. Water droplets applied to the as-treated surfaces spread rapidly, their indicating improved surface wettability.

Table 1. Contact angle degrees of both treated and untreated PP NW samples

Sample	**t=0s (left)**	**t=3s (right)**	**t=0s (left)**	**t=3s (right)**
Washed untreated NW	140,36	139,53	139,03	138,73
Commercial formulation-1 treated NW	115,90	117.50	65,86	64,99
Commercial formulation-2 treated NW	107,59	109,15	19,57	21,97
PPrOz Treated NW	137,78	138,24	137,72	137,26
1% S-PPrOZ-PEI treated NW	122.05	118.57	117.98	115.73

The contact angle measurements provided quantitative insights into the wettability performance of the formulations applied on PP NW substrates. Here, the untreated and simply washed PP NWs exhibited contact angles greater than 139°, affirming their inherent hydrophobicity. Additionally, the treatment with the PPrOZ homopolymer slightly reduced the contact angle to ~137°, suggesting limited surface interactions due to the polymer’s amphiphilic but mostly hydrophobic character. In contrast, the S-PPrOZ-PEI-coated surfaces demonstrated a substantial reduction in contact angle (122.05° at t = 0 s, 115.73° at t = 3 s), revealing their enhanced surface hydrophilicity.

When compared with two commercial hydrophilic coatings, S-PPrOZ-PEI showed competitive yet moderate performance. The commercial formulation-2 resulted in the lowest contact angle of 19.57°, indicating rapid water spreading likely due to the presence of high-density hydrophilic or surfactant groups. However, it is worth noting that such formulations may exhibit lower durability or biocompatibility compared to polyoxazoline-based coatings, which offer both a balance in functionality and the environmental compatibility.

The results demonstrate that the introduction of carboxylic acid groups onto the PPrOZ backbone via succinylation significantly improves surface wettability, positioning S-PPrOZ-PEI as a promising eco-friendly alternative for polymeric surface's modification. The controlled tunability of hydrophilicity through partial hydrolysis and further functionalization possibility underscores the potential of poly(oxazoline) chemistry for advanced surface engineering applications.

IV. CONCLUSIONS

In this study, a new PPrOZ homopolymer was successfully synthesized, and then post-functionalized through both partial hydrolysis and subsequent succinylation to obtain carboxylated polyethylenimine-based derivatives. Her the as-prepared sample's structural characterization by ^{1}H NMR and FTIR confirmed the efficiency of each modification step. The final product, S-PPrOZ-PEI, demonstrated significantly improved wettability performance on PP NW surfaces compared to the unmodified polymer.

The contact angle results revealed that the carboxylic acid functionalization effectively enhanced the surface hydrophilicity, though not to the extent of commercial hydrophilic coatings. However, the poly(oxazoline)-based formulation offers advantages in terms of chemical tunability, potential biocompatibility, as well as the environmental safety. These findings support the potential of S-PPrOZ-PEI as a promising candidate for hydrophilic surface modification of polymeric materials.

ACKNOWLEDGMENTS

This study was supported by Türkiye Bilimsel ve Teknolojik Araştırma Kurumu; Scientific and Technological Research Council of Turkey (TÜBİTAK), Grant Numbers: 5220091, 118C047

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