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Thiourea Polyurethane Composite Modified with Benzaldehyde and its Antimicrobial Properties

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Abstract

New biologically active polyurethane composites were prepared by surface modification of polyurethane foams with thiourea and benzaldehyde. The current work introduces an efficient antimicrobial composite of thiourea polyurethane foam/benzaldehyde (TPU/Benzaldehyde). The main techniques used for thiourea polyurethane foam/benzaldehyde composites identification were Infrared spectra, Ultraviolet-Visible spectra, bandgap energy, X-ray diffraction, Scanning electron microscopy, magnetic susceptibility, and pH of zero-point charge (PHZPC). Surface functions such as carboxylic, lactonic, and phenolic hydroxyl groups have been identified via Boehm titration. The chemical stability of TPU/Benzaldehyde was tested in diverse buffer solutions (pH: 2–14) and various organic solvents (e.g., CH_3OH, CH_3COCH_3, C_6H_6, $C_6H_5CH_3$, DMF, and DMSO). The weights of TPU/Benzaldehyde were unaffected, which confirm its chemical stability. TPU/Benzaldehyde was tested for antibacterial and antifungal activity against Gram-negative bacterium *E. coli*, Gram-positive bacterium *B. cereus*, and fungus *A. niger*. TPU/Benzaldehyde had higher inhibition zones against Gram-positive *B. cereus* than Gram-negative *E. coli*, with inhibition zones of 18±0.03 and 16±0.03 mm, respectively. Also, TPU/Benzaldehyde had higher antifungal action against *A. niger*, with inhibition zones of 20±0.24 mm, than the standard antifungal agent, Fluconazole (14±0.14 mm).

Keywords: Benzaldehyde, thiourea polyurethane foam; Bacillus cereus; Escherichia coli; Aspergillus niger.

Introduction

Polyurethane foam (PUF) is a low-cost substance with a large surface area that can be safe. PUF is primarily employed in many applications, including food packing and transfer (Qiao et al., 2017). PUF can be utilized as an antibacterial agent storage material as well as cold and heat insulation (Sienkiewicz & Czonka, 2022). Polyurethane is already employed in a variety of medical applications, including catheters, surgical drapes, and wound dressing (Borcan et al., 2020).

Thiourea derivatives have lately attracted a lot of attention for their use in the synthesis of a wide range of physiologically active molecules (Elmali et al., 2011). Thiourea derivatives have biological activity owing to the presence of nitrogen and sulfur. Antibacterial, antifungal, anti-inflammatory, antioxidant, and anticancer properties have been reported (Arslan et al., 2009; El-Zahed et al., 2023; Faihan et al., 2021).

Phenols are typically composed of one or more benzene rings and one or more hydroxyl group(s). Phenols are an important chemical family of phytochemicals that have long been recognized for their antibacterial properties (Maisch et al., 2022). The remarkable permeability of phenolic chemicals through the bacterial cell wall may because of their antibacterial effect. Phenols interact with the cell surface, causing cell death by membrane breakdown and the release of internal contents (Alamri et al., 2012). The presence of a hydroxyl group, as well as the amount and location of the hydroxyl groups, were crucial for enhancing antibacterial action further (Huang et al., 2014).

The food and drug administration categorized benzaldehyde as a safe ingredient, and it was utilized as a flavoring substance in foods in the European Union (Gao et al., 2022). Benzaldehyde derivatives, which are phenol analogues, was frequently employed as environmentally friendly antibacterial agents (Alamri et al., 2012). Benzaldehydes suppress fungal development by targeting cellular anti-oxidation components of fungi such as superoxide dismutase, glutathione reductase, and others. They have antifungal properties that can improve the efficiency of standard antifungal drugs (Kim et al., 2011).

Foodborne contamination is often caused by bacteria and fungi. Fever, headache, vomiting, and body pains are typical symptoms of foodborne disease that develop 12 to 72 hours after consuming contaminated food (Switaj et al., 2015; Vats & Nigam, 2022). Antimicrobial compound creation is a high priority field of study since it might be an alternate strategy to combat medication resistance in many microorganisms (Ansari et al., 2013).

Bacillus cereus is a Gram-positive aerobic bacterium, a spore-forming, motile bacterium that can germinate, grow even after being exposed to heat, and create enterotoxins that cause food poisoning (Limban et al., 2018). While *Escherichia coli* is a Gram-negative facultative anaerobic bacterium that resides in people's intestines. Because *E. coli* is often prevalent in the environment, it may readily contaminate food (Limban et al., 2018). *E. coli* may be utilized to detect fecal contamination and can cause serious infections when consumed in contaminated foods (Ma et al., 2023). The Gram-positive bacteria cell wall structure allows hydrophobic chemicals to readily infiltrate the cells and act on both the cell wall and the cytoplasm. Gram-negative bacteria have a peptidoglycan layer (2-3 nm) that is thinner than the peptidoglycan layer in gram-positive bacteria's cell wall. The existence of an outer membrane (OM) is one of the characteristics that distinguishes gram-negative bacteria from gram-positive bacteria. It is made up of a double layer of phospholipids connected to the inner membrane by lipopolysaccharides (LPS).

An OM that comprises different proteins as well as LPS covers the peptidoglycan layer. LPS is made up of lipid A, the core polysaccharide, and the O-side chain, which supplies the "quid" that makes gram-negative bacteria resistant to antimicrobial action (Nazzaro et al., 2013).

On the other hand, fungal infections are a serious public health concern due to the rapid development of antifungal medication resistance (Limban et al., 2018; Ribeiro et al., 2021). *Aspergillus niger* is a fungus that can cause significant infections (Jahani et al., 2020; Latgé, 1999). Mycotoxins and aflatoxins are produced by *A. niger*, a frequent food contamination. *A. niger* can cause aspergillosis, a lung infection that affects the human respiratory system (Gurunathan et al., 2022; Navale et al., 2021; Sheikh-Ali et al., 2014).

The aim of this research is to create antimicrobial polyurethane foams containing thiourea and benzaldehyde for use as wound dressing materials. The phenolic and thiourea functional groups were added to TPU/Benzaldehyde foams. TPU/Benzaldehyde foams were tested for antibacterial activity in vitro against Gram-negative bacteria *E. coli*, Gram-positive bacteria *B. cereus*, and fungus *A. niger*.

Materials and methods

Materials and Reagents

TPU/Benzaldehyde: Flexible PUF sheets (d = 12 kg/m3) were purchased commercially from Foamex Company in New Damietta, Egypt. Benzaldehyde ($C_6H_5.CHO$), Ethanol 70 % (C_2H_6O), Methanol (CH_3OH), Acetone (CH_3COCH_3) and Benzene (C_6H_6) were purchased from Alfa Chemika (Egypt). NH_4SCN, HCl, NaOH, $NaHCO_3$ and Na_2CO_3 were purchased from Sigma-Aldrich (Egypt).

Apparatus

IR spectra of KBr disc were taken with a JASCO IR-410 spectrometer (Germany) in the 4000-400 cm^{-1} range. The JASCO UV/VIS Spectrometer V-630 (Japan) was used to measure all absorbances. The pH was measured using a JENWAY 3510 pH-meter (UK). The X-ray diffraction (XRD) patterns were recorded using X-ray powder diffractometer (Philips, D8-Brucker model), equipped with Ni filter and Cu kα-radiation (λ= 1.5418 Å) at 40 kV and 30 mA. SEM analysis were carried out using a JEOL (JSM-6510LV model, USA), operating at 20 kV in the secondary electron mode.

Methods

Preparation and characterization of TPU/Benzaldehyde

10 g of polyurethane foam (PUF) cubes were cooked in HCl (1 mol/L) with stirring for 3 hours before being thoroughly rinsed with distilled water. PUF cubes were washed in 50 mL of concentrated HCl before being immersed in 25 mL of NH_4SCN solution (5 g/L) (Moawed et al., 2022). Overnight, thiourea polyurethane foam (TPU) was rinsed and air dried. 4 g TPU was refluxed in 200 mL benzaldehyde for 2 hours at 60 °C. TPU/Benzaldehyde was rinsed, dried, and mixed overnight.

TPU/Benzaldehyde was characterized by FTIR, UV-Vis, bandgap energy, magnetic susceptibility, and pH of zero-point charge (PH_{ZPC}). TPU/Benzaldehyde FTIR spectrum was measured between 400 and 4000 cm^{-1}. TPU/Benzaldehyde UV/Vis measurements were taken between 200 and 900 nm. TPU/Benzaldehyde band gap energy (Eg) was calculated using the T_{auc} equation; $(\alpha h\upsilon)^2 = C\,(Eg - h\upsilon)$. Where C denotes a constant. The energy hυ (eV) was computed ($h\upsilon = 1240/\lambda$), where λ is the wavelength in nanometers. α is the absorption coefficient ($\alpha = 2.303\ A/t$), where A is the absorbance and t is the thickness. Boehm's titration was used to determine the total acidic and basic groups of TPU/Benzaldehyde. For 24 hours, 0.5 gm of TPU/Benzaldehyde was soaked in 0.05 M solutions of $NaHCO_3$, Na_2CO_3, NaOH, and HCl. The solutions were then titrated against 0.05 M HCl and NaOH solutions.

The surface charge of TPU/Benzaldehyde was examined throughout a pH range of 2-14, and the pH at zero charge point (pH_{PZC}) was calculated. After soaking 0.5 gm of TPU/Benzaldehyde in each buffer solution for 24 hours, the pH was determined.

TPU/Benzaldehyde magnetic susceptibility (χ_g) was calculated using Evans balance readings using the equation: $\chi_g = CL\,(R - R_0)/10^9(M - M_0)$. Where C is a constant equal to 1.35 cm, L (cm) is the sample height, R is the sample in tube reading, R_o is the empty tube reading, M_0 (gm) is the sample mass, and M0 (gm) is the empty tube mass.

TPU/Benzaldehyde chemical stability was tested in several buffer solutions (pH: 2-14) and organic solvents (e.g., CH_3OH, CH_3COCH_3, C_6H_6, C_6H_5CH3, DMF, and DMSO). TPU/Benzaldehyde was originally weighted, then soaked for 24 hours in each solution and solvent before being filtrated, dried, and weighted.

Antimicrobial activity evaluation using agar well diffusion method

The antimicrobial activity of TPU/Benzaldehyde against *E. coli*, *B. cereus*, and *A. niger* was evaluated using the agar well-diffusion method. The Laboratory Standards Institute recommended using the agar well-diffusion method (2016; Balouiri et al., 2016). Nutrient broth, Nutrient agar, and Dox agar were sterilized for 15 minutes at 121°C. The microbial cultures were adjusted to 0.5 McFarland standards from bacteria (1-2×10^8 CFU/ml) or 10^6 CFU/ml from fungal spore suspension and injected into the agar media specifically (100 µl). In triplicate, sterile Petri plates were filled with inoculated agar material. A sterile corkborer was used to make tiny wells of 5 mm after the medium solidification. Then, individually, 300 µg/ml of TPU/Benzaldehyde, Penicillin (antibacterial), and Fluconazole (antifungal) in DMF were added to the tiny wells. Dox agar plates were incubated at 30 °C for 5 days, whereas nutrient agar plates were incubated at 37 °C for 24 hours. Zones of inhibition of TPU/Benzaldehyde and Standard deviation (SD) after incubation were measured in millimeters (mm).

Minimum inhibition concentration (MIC)

TPU/Benzaldehyde MIC was examined against *E. coli*, *B. cereus* and *A. niger* (El-Fallal et al., 2023). Nutrient broth and Dox broth was prepared, autoclaved for 15 minutes at 121°C, and coaled at 47°C. 100 µl of *E. coli* and *B. cereus* (0.5 McFarland standards ($1\text{-}2\times10^8$ CFU/ml) and 10^6 CFU/ml of *A. niger* spore suspension were injected in two sets of flasks. Each flask was carefully filled with varying amounts of sorbent (0-1000 µg/ml), with one acting as a positive control to observe the normal growth of the microbial cells in the absence of TPU/Benzaldehyde. A negative control flask with only cells and DMF was also performed. The flasks were incubated in a shaker incubator (100 rpm) at 37°C for 24 hours or 30°C for 5 days for bacteria or fungi, respectively. The turbidity of the bacterial broth indicated the formation of the inoculums in the broth, and the MIC was determined spectrophotometrically at 600 nm as the lowest concentration of TPU/Benzaldehyde that inhibited the growth of the test bacteria. For fungus, the fungal biomass was filtered using Whatman filter paper No.1, dried and the dry weight (g) was determined.

Statistical analysis

Using SPSS software version 18, the data were analyzed using the ANOVA test. The significance difference was set at $p \leq 0.05$. The experiments were carried out three times. The mean and standard deviation (SD) were also calculated.

Results

Characterization of TPU/Benzaldehyde

The main functional groups of TPU/Benzaldehyde were identified using IR spectrum, which recorded in the range of 400 and 4000 cm^{-1}. The absorption peaks of TPU/Benzaldehyde were observed at 3740-2941, 2919, 2850, 2042, 1619 and 1116 cm^{-1} (Figure 1(A)). A broadband of –NH and –OH groups was observed at 3740-2941 cm^{-1}. Several peaks were observed at 2919, 2850 (–CH), 2042 (N=C=S), 1619 (C=C) and 1116 cm^{-1} (C–O). While the characteristic absorption peaks of PUF were observed at 3777, 3272 (–OH and –NH), 2866 (–CH), 1671 (C=O), 1633(C=C), 1543 (N–O) and 1217 (C–O) cm^{-1} (Figure 1(B)).

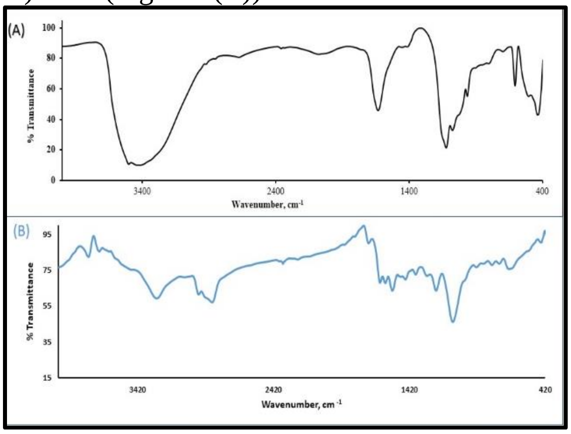

Figure 1. (A) IR spectrum of TPU/Benzaldehyde. (B) IR spectrum of PUF.

UV-Vis absorption spectrum of TPU/Benzaldehyde was carried out in the solid state using Nujol mulls method (Figure 2(A)). The specific absorption peaks of TPU/Benzaldehyde were observed at 241, 250, 274, 277, 280, 290, 340 and 370 nm. TPU/Benzaldehyde absorbs light at maximum wavelength λ_{max} = 241 nm, assigned to the transition π-π^*. The presence of less intense absorption peaks in the 250 to 277 nm is an indication of the aromatic ring. In comparison, UV-Vis spectrum of PUF (Figure 2(B)) were absorbs light at maximum wavelength λ_{max} = 261 nm.

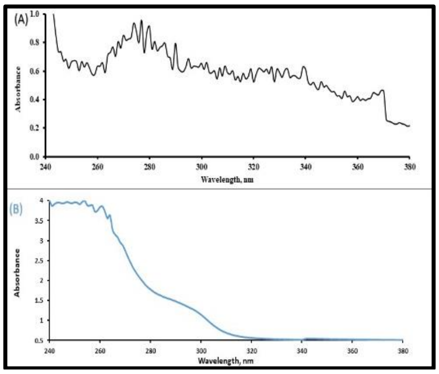

Figure 2. (A) UV-Vis spectrum of TPU/Benzaldehyde. (B) UV-Vis spectrum of PUF.

The bandgap energy (E_g) of TPU/Benzaldehyde was determined from UV-Vis measurements using Tauc equation. The $(\alpha h\upsilon)^2$ were plotted against hυ and the energy gap can be approximated from the straight portion of the hυ axis at hυ = 0. The bandgap energy of TPU/Benzaldehyde was estimated as 2.85 eV (Figure 3).

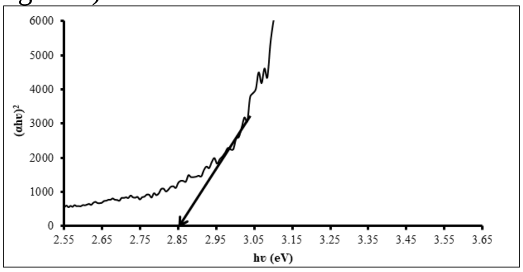

Figure 3. Bandgap energy of TPU/Benzaldehyde

The surface charge of TPU/Benzaldehyde at different pH and pH at zero charge point (pH_{PZC}) were evaluated. The differences between the initial and final pH values ($\Delta pH = pH_f - pH_i$) were plotted against the initial pH. The pH_{PZC} of TPU/Benzaldehyde was found 4.05 (Figure 4).

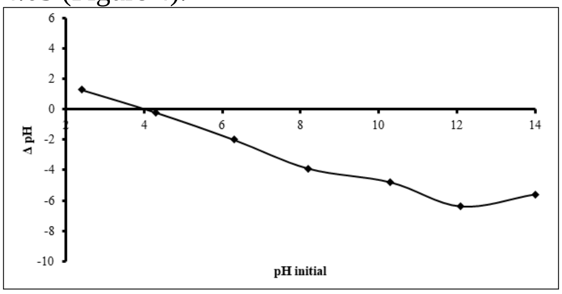

Figure 4. pH_{PZC} of TPU/Benzaldehyde

The X-ray diffraction patterns of TPU/Benzaldehyde were appeared as amorphous structure with no crystalline diffraction peaks (Figure 5). The broad diffraction bands at 2θ, 22.5° were characteristic for PUF and the amorphous character for the aromatic TPU/Benzaldehyde was also observed.

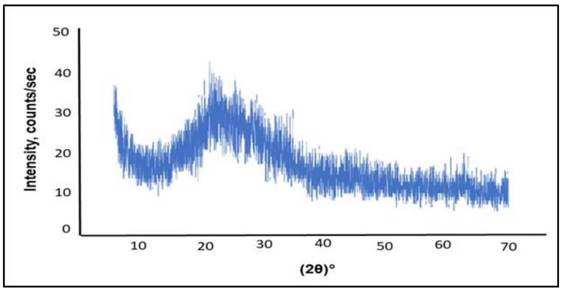

Figure 5. XRD of TPU/Benzaldehyde

The surface morphology of TPU/Benzaldehyde were characterized using SEM image at magnifications 15,000 x (Figure 6). SEM image were identified the irregular size and shape of TPU/Benzaldehyde.

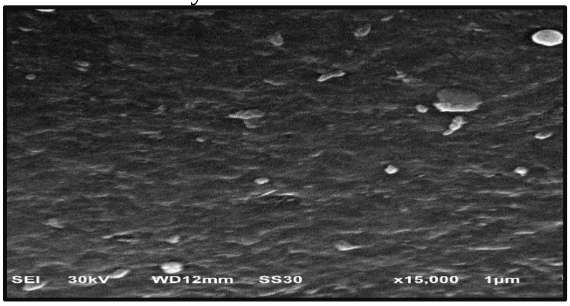

Figure 6. SEM of TPU/Benzaldehyde

The magnetic susceptibility χ_g of TPU/Benzaldehyde was determined using Evans balance data. TPU/Benzaldehyde magnetic susceptibility was -1.13 × 10^{-6} cm^3/mol, which is extremely low and negative. TPU/Benzaldehyde was regarded a diamagnetic material with a negative magnetic susceptibility (Table 1).

Table 1. Magnetic susceptibility of TPU/Benzaldehyde

Sorbent	C	L	R_s	R_0	M_s	M_0	χ_g
TPU/ Benzaldehyde	1.35	1.8	-32	-29	0.7555	0.7491	- 1.13 × 10^{-6}

The chemical stability of TPU/Benzaldehyde was tested in diverse buffer solutions (pH: 2–14) and various organic solvents (e.g., CH_3OH, CH_3COCH_3, C_6H_6, C_6H_5CH3, DMF, and DMSO). The weights of TPU/Benzaldehyde were unaffected, which confirm its chemical stability.

Antimicrobial activity evaluation

TPU/Benzaldehyde was tested for antibacterial efficacy against Gram-negative bacteria *E. coli*, Gram-positive bacteria *B. cereus*, and fungus *A. niger*. The zone of inhibition (ZOI) of TPU/Benzaldehyde against *E. coli*, *B. cereus*, and *A. niger* was calculated using the agar well diffusion method (Figure 7).

Employing the agar well diffusion technique against *B. cereus*, *E. coli*, and *A. niger* in contrast to Penicillin (standard antibacterial) and Fluconazole (standard antifungal). The diameter of inhibitory zones (mm) is indicated by arrows. TPU/Benzaldehyde inhibited Gram-positive *B. cereus* better than Gram-negative *E. coli*, with inhibition zones of 18±0.03 and 16±0.03 mm, respectively. Penicillin was more effective against bacteria, with inhibition zones of 40±0 mm against *E. coli* and 25±0.03 mm against *B. cereus*. Furthermore, TPU/Benzaldehyde has a greater antifungal activity against *A. niger* (20±0.24 mm) than Fluconazole (14±0.14 mm) (Table 2).

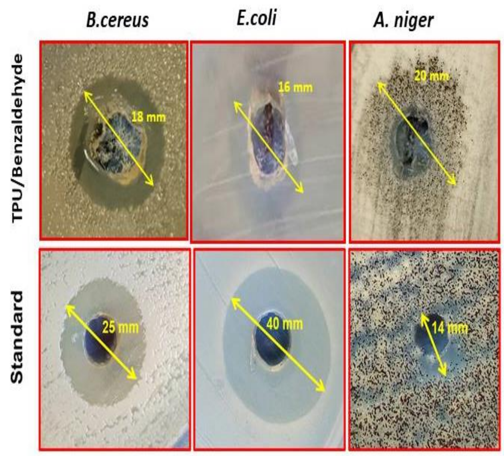

Figure 7. Antimicrobial activity of TPU/Benzaldehyde

Table 2. Zones of inhibition (ZOI) of TPU/Benzaldehyde in comparison with Penicillin (standard antibacterial) and Fluconazole (standard antifungal)

Compound	**Zones of inhibition (mm ± SE)**		
	E. coli	*B. cereus*	*A. niger*
TPU/Benzaldehyde	16 ± 0.03	18 ± 0.03	20 ± 0.24
Penicillin	40 ± 0	25 ± 0.03	-
Fluconazole	-	-	14 ± 0.14

TPU/Benzaldehyde revealed MIC values of 90, 130 and 60 µg/ml against *E. coli*, *B. cereus* and *A. niger* as shown in Figure 8. These results showed that the TPU/Benzaldehyde was better antifungal activity than antibacterial activity and better antibacterial action against Gram-negative than Gram-positive bacteria.

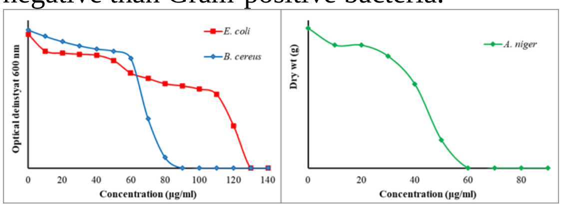

Figure 8. Minimum inhibition concentration of TPU/Benzaldehyde against *E. coli*, *B. cereus* and *A. niger*.

Discussion

Microbial infections continue to be a major source of morbidity and death. The rising worry about multidrug-resistant bacterial strains, biofilm-associated diseases and developed fungal resistance necessitates the development of new bactericidal and fungicidal agents (Sharma et al., 2023). As a result, novel and developing polymer-based materials in antimicrobial chemotherapy was received significant attention. Thiourea and benzaldehyde was extensively researched for their antibacterial and antifungal properties (Khan et al., 2021). They are microbicidal owing to the formation of reactive oxygen species (ROS) (Pan et al., 2010). The current work aimed to fabricate thiourea polyurethane composite modified with benzaldehyde and investigate its antimicrobial potential.

Different techniques used for the characterization of TPU/Benzaldehyde composites including Infrared spectra, Ultraviolet-Visible spectra, bandgap energy, X-ray diffraction, Scanning electron microscopy, magnetic susceptibility, and pH of zero-point charge (PH_{ZPC}). The recorded main functional groups of TPU/Benzaldehyde were related to –NH, –OH, –CH, N=C=S, C=C and C–O groups according to the IR spectrum, which confirmed the successful synthesis of TPU/Benzaldehyde (Singh et al., 2020). Also, UV-Vis absorption spectrum of TPU/Benzaldehyde revealed specific absorption peaks at 218, 226-239, 241, 290 and 370 nm (Samarasinghe et al., 2018).
The pH of zero-point charge (pH_{PZC}) measurement was helped in predicting the surface behavior of composite which was 4.05 (Boumediene et al., 2018). The surface of TPU/Benzaldehyde will be positively charged at pH< 4.05 and negatively charged at pH > 4.05.

Surface functions such as carboxylic, lactonic, and phenolic hydroxyl groups have been identified via Boehm titration. Sodium hydroxide (NaOH) neutralizes all three functionalities, while sodium carbonate (Na_2CO_3) neutralizes carboxylic and phenolic groups and sodium bicarbonate ($NaHCO_3$) only neutralizes phenolic groups (Kim et al., 2011; Schönherr et al., 2018). TPU/Benzaldehyde acidic sites were 27 mmol/g, whereas basic sites were insignificant.
Magnetic susceptibility is a physical parameter that is commonly used to characterize para and dia magnetic materials. When biological tissue is subjected to a magnetic field, it produces a unique magnetic field pattern that is mirrored in its interactions with materials (Schweser et al., 2010).

The antibacterial and antifungal efficiency of TPU/Benzaldehyde was evaluated against Gram-negative bacterium *E. coli*, Gram-positive bacterium *B. cereus*, and the fungus *A. niger*. TPU/Benzaldehyde showed a good antimicrobial action against *E. coli*, *B. cereus* and *A. niger* with MIC values reached to 90, 130 and 60 µg/ml. While Bhadani et al. (2015) found that 40-160 µg/ml of benzaldehyde and thiourea/urea derivatives were enough to inhibit *E. coli* and *S. aureus*. On the other hand, Fathalla et al. (2005) reported that thiourea derivatives showed MIC against *E. coli* was 412 µg/ml and against *B. subtilis* was 1250 µg/ml.

Also, thioureas and their cyclized derivatives showed MIC values ranged from 200-1024 µg/ml against *E. coli* as recorded by Tuncel et al. (2019). TPU/Benzaldehyde antibacterial activity was tested in terms of surface charging behavior, production of ROS, changes in membrane permeability, and disruption of cell wall structure. Bacterial cell walls contain a negative charge because acidic substances like peptidoglycan are present (Schleifer & Kandler, 1972). As the characterization findings were accepted, the surface charge of TPU/Benzaldehyde was mostly acidic. A repulsive force may be generated between TPU/Benzaldehyde and the bacterial cells, reducing TPU/Benzaldehyde's antibacterial activity in comparison to the usual antibacterial agent (Penicillin).

With inhibition zones of 18 0.03 mm, TPU/Benzaldehyde demonstrated strong antibacterial activity against Gram-positive *B. cereus*. The principal mechanism of action on *B. cereus* was cell wall disintegration. Gram-positive bacteria have greater negative charge values in their cell walls due to bigger peptidoglycan coats. The development of oxidative stress in microbial cells is one of the most commonly cited processes of cell wall disintegration. ROS may be produced inside cells, causing stress in microbial cells causing damage to cellular structures and outer layers, including oxidative degradation of proteins and lipids and ultimately leading to cell death (Metryka et al., 2021).

TPU/Benzaldehyde showed effective antibacterial activity against Gram-negative *E. coli*, with inhibition zones of 16±0.03 mm. Membrane permeability change is the principal mode of action against Gram-negative bacteria (*E. coli*). The presence of a low-density zone in the cytoplasm of *E. coli* cells shows that the permeability of the cytoplasmic membrane can be altered, hence disrupting cellular function (Huang et al., 2017).

TPU/Benzaldehyde causes damage to the integrity of cell membranes, resulting in cell component leakage and the production of oxidative stress. *Bacillus* spp. increased ROS, which cause irreversible cell damage, explaining why TPU/Benzaldehyde was more effective against *B. cereus* than *E. coli*. The mechanism of Benzaldehyde as a volatile organic molecule (VOC) comprises disruption to cell membrane integrity, resulting in cell component leakage and oxidative stress (Gao et al., 2022). *Bacillus spp.*-produced VOCs caused an increase in ROS of *Sclerotinia sclerotiorum* hyphae cells structural defects in cell walls cytoplasm and multivesicular structure disruption, possibly due to oxidative stress (Massawe et al., 2018). In terms of biocidal effect against bacteria, benzaldehydes are similar to phenols. They interact with the cell's surface, causing cell death by membrane breakdown and the release of internal contents. Benzaldehydes also produce intracellular cytoplasmic coagulation, which results in cell death or suppression of cell development (Alamri et al., 2012). Many thiourea compounds also showed antibacterial activity against *B. cereus* and *E. coli* (Marzi et al., 2019).

Furthermore, TPU/Benzaldehyde showed greater antifungal activity against *A. niger* (20±0.24 mm) than Fluconazole (14±0.14 mm). TPU/Benzaldehyde reduces spore germination and deactivates spores, which is necessary to prevent fungal infection and mycotoxin generation. The rupture of cell walls and membranes, resulting in microbial morphological alterations, is the fundamental mechanism underpinning TPU/Benzaldehyde's antifungal actions. Benzaldehydes targeting cellular antioxidation components of fungi, such as superoxide dismutase, glutathione reductase, and others, efficiently limit fungal development (Kim et al., 2011). The rupture of cell wall and membrane structures caused intracellular lysate leakage and the production of oxidative stress (Gao et al., 2022; Zhao et al., 2022). Furthermore, various thiourea compounds showed antifungal activity against *A. niger* (Limban et al., 2018; Limban et al., 2020).

Conclusion

By combining Benzaldehyde and Thiourea polyurethane foam, Benzaldehyde Thiourea polyurethane foam (TPU/Benzaldehyde) was created. IR, UV/Vis, bandgap energy, XRD, SEM, magnetic susceptibility, chemical stability, and pH_{PZC} were all used to characterize TPU/Benzaldehyde. TPU/Benzaldehyde antibacterial activity was investigated in vitro against *E. coli*, *B. cereus*, and *A. niger*. TPU/Benzaldehyde showed a stronger antibacterial effect on Gram-positive *B. cereus* than on Gram-negative *E. coli*. TPU/Benzaldehyde outperformed Fluconazole in antifungal activity against *A. niger*. TPU/Benzaldehyde might be employed as an antibacterial agent in future industrial and biological applications.

References

Alamri, A., El-Newehy, M. H., & Al-Deyab, S. S. (2012). Biocidal polymers: synthesis and antimicrobial properties of benzaldehyde derivatives immobilized onto amine-terminated polyacrylonitrile. Chemistry Central Journal, 6(1), 1-13.

Ansari, M. A., Khan, H. M., Khan, A. A., Pal, R., & Cameotra, S. S. (2013). Antibacterial potential of Al 2 O 3 nanoparticles against multidrug resistance strains of Staphylococcus aureus isolated from skin exudates. Journal of nanoparticle research, 15, 1-12.

Arslan, H., Duran, N., Borekci, G., Koray Ozer, C., & Akbay, C. (2009). Antimicrobial activity of some thiourea derivatives and their nickel and copper complexes. Molecules, 14(1), 519-527.

Balouiri, M., Sadiki, M., & Ibnsouda, S. K. (2016). Methods for in vitro evaluating antimicrobial activity: A review. Journal of pharmaceutical analysis, 6(2), 71-79.

Bhadani, V. N., Patel, P. A., Purohit, H. D., & Purohit, D. M. (2015). Synthesis, antibacterial and antifungal activity of 5-aryl amido-6-isopropyl-2-(mercapto/hydroxy)-4-[(4′-difluoro methoxy)(3′-hydroxy) phenyl]-1, 4-dihydro pyrimidine. International Letters of Chemistry, Physics and Astronomy, 51, 55.

Borcan, F., Mioc, M., Ghiulai, R., Pinzaru, I., Dehelean, C. A., & Soica, C. M. (2020). A Study on the Behavior of a Polyurethane Drug Carrier in Various pH Media. Journal of Medicine and Life, 13(2), 195.

Boumediene, M., Benaïssa, H., George, B., Molina, S., & Merlin, A. (2018). Effects of pH and ionic strength on methylene blue removal from synthetic aqueous solutions by sorption onto orange peel and desorption study. J. Mater. Environ. Sci, 9(6), 1700-1711.

El-Fallal, A. A., Elfayoumy, R. A., & El-Zahed, M. M. (2023). Antibacterial activity of biosynthesized zinc oxide nanoparticles using Kombucha extract. SN Applied Sciences, 5(12), 332.

Elmali, F. T., Avciata, U., & Demirhan, N. (2011). Synthesis and characterization of new thiourea derivatives substituted 1, 10-phenanthroline and crown ether. Main Group Chemistry, 10(1), 17-23.

El-Zahed, M. M., Kiwaan, H. A., Farhat, A. A., Moawed, E. A., & El-Sonbati, M. A. (2023). Anticandidal action of polyurethane foam: a new modifier with functionalized isothiouronium group. Iranian Polymer Journal, 32(1), 71-79. doi:https://doi.org/10.1007/s13726-022-01112-1

Faihan, A. S., Hatshan, M. R., Kadhim, M. M., Alqahtani, A. S., Nasr, F. A., Saleh, A. M., . . . Al-Janabi, A. S. (2021). Promising bio-active complexes of platinum (II) and palladium (II) derived from heterocyclic thiourea: Synthesis, characterization, DFT, molecular docking, and anti-cancer studies. doi:https://doi.org/10.1016/j.molstruc.2021.132198

Fathalla, O. A., Awad, S. M., & Mohamed, M. S. (2005). Synthesis of new 2-thiouracil-5-sulphonamide derivatives with antibacterial and antifungal activity. Archives of pharmacal research, 28, 1205-1212.

Gao, Y., Ren, H., He, S., Duan, S., Xing, S., Li, X., & Huang, Q. (2022). Antifungal activity of the volatile organic compounds produced by Ceratocystis fimbriata strains WSJK-1 and Mby. Frontiers in Microbiology, 13, 1034939.

Gurunathan, S., Lee, A. R., & Kim, J. H. (2022). Antifungal effect of nanoparticles against COVID-19 linked black fungus: a perspective on biomedical applications. International Journal of Molecular Sciences, 23(20), 12526.

Huang, S., Zhang, C.-P., Li, G. Q., Sun, Y.-Y., Wang, K., & Hu, F.-L. (2014). Identification of catechol as a new marker for detecting propolis adulteration. Molecules, 19(7), 10208-10217.

Huang, X., Bao, X., Liu, Y., Wang, Z., & Hu, Q. (2017). Catechol-functional chitosan/silver nanoparticle composite as a highly effective antibacterial agent with species-specific mechanisms. Scientific reports, 7(1), 1860.

Jaafar, A., Mansour, N., Fix-Tailler, A., Allain, M., Faour, W. H., Shebaby, W. N., . . . Larcher, G. (2022). Synthesis, Characterization, Antibacterial and Antifungal Activities Evaluation of Metal Complexes With

Benzaldehyde-4-methylthiosemicarbazone Derivatives. ChemistrySelect, 7(10), e202104497.

Jahani, M., Pira, M., & Aminifard, M. H. (2020). Antifungal effects of essential oils against Aspergillus niger in vitro and in vivo on pomegranate (Punica granatum) fruits. Scientia Horticulturae, 264, 109188.

Khan, E., Khan, S., Gul, Z., & Muhammad, M. (2021). Medicinal importance, coordination chemistry with selected metals (cu, Ag, au) and Chemosensing of Thiourea derivatives. A review. Critical Reviews in Analytical Chemistry, 51(8), 812-834.

Kim, J. H., Chan, K. L., Mahoney, N., & Campbell, B. C. (2011). Antifungal activity of redox-active benzaldehydes that target cellular antioxidation. Annals of clinical microbiology and antimicrobials, 10, 1-16.

Kim, Y., Yang, S., Kim, S., Lim, H., Kim, T., & Park, C. (2011). Standaridization of Boehm titration analysis of surface functionalities of CNTs as reinforcements for composites. Paper presented at the 18 TH International conference on composite materials: ICC, Jeju Island [Korea].

Latgé, J.-P. (1999). Aspergillus fumigatus and aspergillosis. Clinical microbiology reviews, 12(2), 310-350.

Limban, C., Chifiriuc, M. C., Caproiu, M. T., Dumitrascu, F., Ferbinteanu, M., Pintilie, L., . . . Marutescu, L. G. (2020). New substituted benzoylthiourea derivatives: from design to antimicrobial applications. Molecules, 25(7), 1478.

Limban, C., Missir, A. V., Caproiu, M. T., Grumezescu, A. M., Chifiriuc, M. C., Bleotu, C., . . . Nuta, D. C. (2018). Novel hybrid formulations based on thiourea derivatives and core@ shell Fe3O4@ C18 nanostructures for the development of antifungal strategies. Nanomaterials, 8(1), 47.

Ma, E., An, Y., Zhang, G., Zhao, M., Iqbal, M. W., Zabed, H. M., & Qi, X. (2023). Enhancing the antibacterial activity of Lactobacillus reuteri against Escherichia coli by random mutagenesis and delineating its mechanism. Food Bioscience, 51, 102209. doi:https://doi.org/10.1016/j.fbio.2022.102209

Maisch, N. A., Bereswill, S., & Heimesaat, M. M. (2022). Antibacterial effects of vanilla ingredients provide novel treatment options for infections with multidrug-resistant bacteria–A recent literature review. European Journal of Microbiology and Immunology, 12(3), 53-62.

Marzi, M., Pourshamsian, K., Hatamjafari, F., Shiroudi, A., & Oliaey, A. (2019). Synthesis of New N-Benzoyl-N'-Triazine Thiourea Derivatives and Their Antibacterial Activity. Russian Journal of Bioorganic Chemistry, 45, 391-397.

Massawe, V. C., Hanif, A., Farzand, A., Mburu, D. K., Ochola, S. O., Wu, L., . . . Gao, X. (2018). Volatile compounds of endophytic Bacillus spp. have biocontrol activity against Sclerotinia sclerotiorum. Phytopathology, 108(12), 1373-1385.

Metryka, O., Wasilkowski, D., & Mrozik, A. (2021). Insight into the antibacterial activity of selected metal nanoparticles and alterations within the antioxidant defence system in Escherichia coli, Bacillus cereus and Staphylococcus epidermidis. International Journal of Molecular Sciences, 22(21), 11811.

Moawed, E., Eissa, M., & Al-Tantawy, S. (2022). Application of polyurethane foam/zinc oxide nanocomposite for antibacterial activity, detection, and removal of basic dyes from wastewater. International Journal of Environmental Science and Technology, 1-8.

Navale, V., Vamkudoth, K. R., Ajmera, S., & Dhuri, V. (2021). Aspergillus derived mycotoxins in food and the environment: Prevalence, detection, and toxicity. Toxicology reports, 8, 1008-1030.

Nazzaro, F., Fratianni, F., De Martino, L., Coppola, R., & De Feo, V. (2013). Effect of essential oils on pathogenic bacteria. Pharmaceuticals, 6(12), 1451-1474.

Pan, X., Redding, J. E., Wiley, P. A., Wen, L., McConnell, J. S., & Zhang, B. (2010). Mutagenicity evaluation of metal oxide nanoparticles by the bacterial reverse mutation assay. Chemosphere, 79(1), 113-116.

Qiao, M., Ren, T., Huang, T.-S., Weese, J., Liu, Y., Ren, X., & Farag, R. (2017). N-Halamine modified thermoplastic polyurethane with rechargeable antimicrobial function for food contact surface. RSC advances, 7(3), 1233-1240. doi:10.1039/C6RA25502G

Ribeiro, A. S., Costa, S. M., Ferreira, D. P., Calhelha, R. C., Barros, L., Stojković, D., . . . Fangueiro, R. (2021). Chitosan/nanocellulose electrospun fibers with enhanced antibacterial and antifungal activity for wound dressing applications. Reactive and Functional Polymers, 159, 104808.

Samarasinghe, W. M. P., Sithambaresan, M., & Mahendranathan, C. (2018). Synthesis, Characterization and Evaluation of Antibacterial Activity of a New Phenylmethylidene Thiourea Derivative and Its Copper (II) Complex. International Journal of Current Innovations in Advanced Research, 59-68.

Schleifer, K. H., & Kandler, O. (1972). Peptidoglycan types of bacterial cell walls and their taxonomic implications. Bacteriological reviews, 36(4), 407-477.

Schönherr, J., Buchheim, J. R., Scholz, P., & Adelhelm, P. (2018). Boehm titration revisited (part i): Practical aspects for achieving a high precision in quantifying oxygen-containing surface groups on carbon materials. C, 4(2), 21.

Schweser, F., Deistung, A., Lehr, B. W., & Reichenbach, J. R. (2010). Differentiation between diamagnetic and paramagnetic cerebral lesions based on magnetic susceptibility mapping. Medical physics, 37(10), 5165-5178.

Sharma, R. P., Shirsat, S. D., Shinde, P. V., Mohite, S. S., & Mane, R. S. (2023). Nano-antimicrobial Materials: Alternative Antimicrobial Approach. In Nanomaterials for Sustainable Development: Opportunities and Future Perspectives (pp. 137-171). Singapore: Springer Nature Singapore.

Sheikh-Ali, S. I., Ahmad, A., Mohd-Setapar, S.-H., Zakaria, Z. A., Abdul-Talib, N., Khamis, A. K., & Hoque, M. E. (2014). The potential hazards of Aspergillus sp. in foods and feeds, and the role of biological treatment: A review. Journal of Microbiology, 52, 807-818. doi:DOI: 10.1007/s12275-014-4294-7

Sienkiewicz, N., & Członka, S. (2022). Natural additives improving polyurethane antimicrobial activity. Polymers, 14(13), 2533.

Singh, V., Singh, S., Verma, A., Choudhary, R. R., & Gupta, S. (2020). Synthesis, Characterization and Electrical Conductivity of Transition Metal Complexes of Tri-Thiocarbonate and Phenol-Thiourea Based Ligand. Solid State Technology, 63(6), 20406-20416.

Switaj, T. L., Winter, K. J., & Christensen, S. (2015). Diagnosis and management of foodborne illness. American family physician, 92(5), 358-365.

Tuncel, S. T., Gunal, S. E., Ekizoglu, M., Kelekci, N. G., Erdem, S. S., Bulak, E., ... & Dogan, I. (2019). Thioureas and their cyclized derivatives: Synthesis, conformational analysis and antimicrobial evaluation. Journal of Molecular Structure, 1179, 40-56.

Vats, A., & Nigam, P. (2022). Microbial Infection Pathogenesis and Progression: A Critical Review. doi:10.5281/zenodo.7002860

Zhao, X., Zhou, J., Tian, R., & Liu, Y. (2022). Microbial volatile organic compounds: Antifungal mechanisms, applications, and challenges. Frontiers in Microbiology, 13, 922450.

الملخص العربي

عنوان البحث: تصنيع مركب ثيوريا بولي يوريثان المعدل بالبنزالديهايد وخصائصه الميكروبية

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تم تحضير مركبات بولي يوريثان نشطة بيولوجيا جديدة عن طريق تعديل سطح البولي يوريثان مع الثيوريا والبنزالدهيد. يقدم العمل الحالي مركبًا فعالًا مضادًا للميكروبات من البولي يوريثان ثيوريا / البنزالديهيد. كانت التقنيات الرئيسية المستخدمة لتوصيف مركب البولي يوريثان/ البنزالديهايد ثيوريا هي طيف الأشعة تحت الحمراء، وطيف الأشعة فوق البنفسجية والمرئية، وطاقة فجوة النطاق، وحيود الأشعة السينية، والقابلية المغناطيسية، ودرجة الحموضة لشحنة نقطة الصفر. تم تقييم التأثير المضاد للميكروبات لـ مركب البولي يوريثان/ البنزالديهايد ضد البكتيريا سالبة الجرام (ايشريشيا كولاي) والبكتيريا إيجابية الجرام (باسيلس سيريس) والفطر(اسبرجيلس نيجر). أظهراختبار انتشار المواد خلال الأجار معمليا مناطق تثبيط أعلى لـ البولي يوريثان/ البنزالديهايد ضد البكتيريا إيجابية الجرام (١٨ ± ٠,٠٣ مم) مقارنة بالبكتريا سالبة الجرام مع مناطق تثبيط (١٦ ± ٠,٠٣ مم)، وأظهر البولي يوريثان/ البنزالديهايد تأثيرًا مضادًا للفطريات أعلى ضد اسبرجيلس نيجر بمناطق تثبيط تبلغ ٢٠ ± ٠,٢٤ مم من العامل المضاد للفطريات القياسي، فلوكونازول (١٤ ± ٠,١٤ مم). يمكن معالجة مركبات البولي يوريثان/ البنزالديهايد النشطة بيولوجيًا الناتجة إلى منتجات للأغراض الطبية والصناعية.