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## TPU membrane containing biodegradable PLA for CO<sub>2</sub>/N<sub>2</sub> separation

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### 1. ABSTRACT

Environmental problems and global warming have actuated the researches on CO<sub>2</sub> separation from flue gas. Membrane technology is a widely used method for CO<sub>2</sub> separation due to simplicity and low energy consumption. The choice of suitable materials for membranes has an important role in the CO<sub>2</sub> separation performance. In this research, a new type of polymeric membrane with high chemical and mechanical properties was prepared for CO<sub>2</sub> separation using biodegradable material. To this end, thermoplastic polyurethane (TPU) was synthesized from its raw materials and then was blended with polylactic acid (PLA). Fourier transform infrared spectroscopy (FTIR), X-ray diffraction patterns (XRD), Atomic force microscopy (AFM), differential scanning calorimetry (DSC) and tensile analysis were used to assess the chemical, physical and mechanical properties of the membranes. These analyses confirmed the chemical structure of the TPU and blends and observed that in the TPU-20%, the degree of crystallization reduced and the glass transition temperature is increased. It was also found that with the addition of PLA, the Tensile strength and Elongation at break increased. The optimum permeability was observed in TPU-20% (80 Barrer) and the better selectivity was obtained in TPU-30% (310). Ultimately, this study yielded a biodegradable membrane exhibiting excellent CO<sub>2</sub> separation capabilities.

**Keywords:** Thermoplastic Polyurethane, Polylactic Acid, CO<sub>2</sub> Separation, Membrane.

### 2. INTRODUCTION (headlines: TNR Bold, 11pt)

Thermoplastic polyurethane (TPU) is an elastomeric polymer that exhibits both thermoplastic and rubber-like properties, making it recyclable and highly processable [1]. TPU has excellent mechanical strength, abrasion resistance, flexibility at low temperatures, and resistance to water, oil, and solvents. When blended with PLA, TPU enhances the blend's flexibility, viscoelasticity, toughness, cold crystallization temperature, viscosity, storage modulus, and melt strength. PLA-TPU blends are utilized in various applications, including biomedical devices, packaging, automotive parts, membranes, sensors, catalysts, and electromagnetic shielding [2]. The final properties of these blends depend on their morphology and crystallinity. To enhance TPU's permeability, researchers have introduced various additives. As a biodegradable and cost-effective polymer, PLA has the potential to improve TPU's membrane separation performance [3].

### 3. MATERIALS AND METHODS

TPU and TPU/PLA membranes were synthesized and then were characterized. Measurement Gas permeability tests were conducted using a flat-sheet module in a constant pressure-variable volume system (Figure 1).

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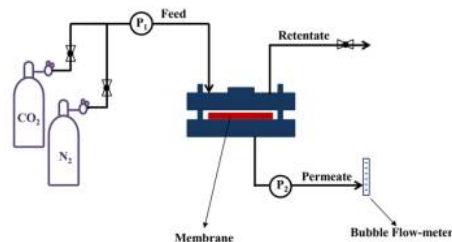


Figure 1. Schematic of gas permeation system

## 4. RESULTS AND DISCUSSION

### 4.1. Characterization

FTIR was used to analyze the chemical structure of TPU and TPU/PLA, with the spectra shown in Figure 2. These confirm the presence of TPU and TPU/PLA structures. The crystalline structure of the polymers was examined using X-ray diffraction (XRD), as shown in Figure 3, with results summarized in Table 1. Crystallinity decreases significantly with increasing PLA content up to 20 wt%, at which point the sample is considered amorphous. Phase images of the membranes (Figure 4) indicate that the addition of PLA induces phase separation within the microphase structure. This effect becomes more pronounced at higher PLA contents, reaching a maximum at 30%. These observations align with XRD results, further confirming changes in crystallinity with PLA incorporation. Differential scanning calorimetry (DSC) was conducted to assess thermal properties (Figure 5, Table 2). Results show that glass transition temperature ( $T_g$ ) increases with PLA content up to 20%. Tensile tests were performed to evaluate mechanical behavior (Figure 6, Table 3).

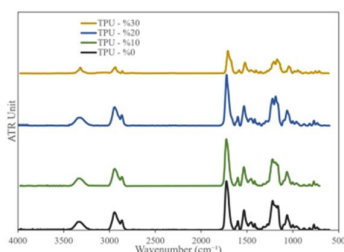


Figure 2. FTIR spectra of prepared membranes

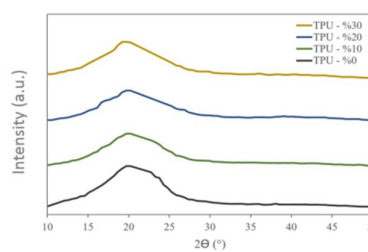


Figure 3. The XRD patterns of the prepared membranes

Table 1. The solubility coefficients of CO<sub>2</sub> and N<sub>2</sub>

Sample	L <sub>110</sub> (nm)	L <sub>200</sub> (nm)	Degree of crystallinity (%)
TPU - %0	34.22	22.91	6.97
TPU - % 10	34.02	18.70	1.13
TPU - %20	15.71	10.01	0.09
TPU - %30	33.25	19.91	4.25

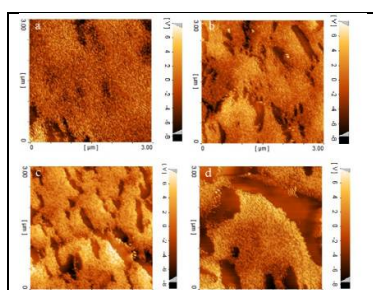


Figure 4. AFM phase images of the membranes

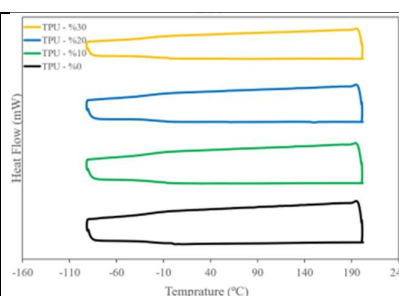


Figure 5. DSC thermograms of the prepared membranes

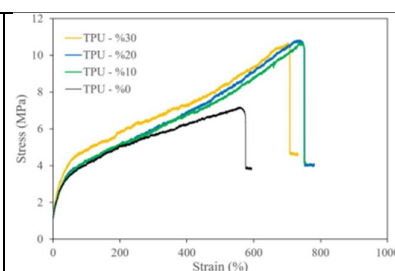


Figure 6. Stress-strain curves of the prepared membranes

Table 2. The  $T_g$  of the prepared membranes

Sample	$T_g$ (soft domain) (°C)
TPU - %0	-20.0
TPU - % 10	-19.1
TPU - %20	-18.9
TPU - %30	-26.0

Table 3. The results of the tensile test of the prepared membranes



Sample	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
TPU - %0	27.15	559.95	7.19
TPU - %10	15.43	738.46	10.67
TPU - %20	21.30	742.78	10.82
TPU - %30	18.65	701.78	10.68

#### 4.2. Gas Separation Properties

The permeability results are shown in Figure 7, and the CO<sub>2</sub>/N<sub>2</sub> selectivity is presented in Figure 8. It is evident that CO<sub>2</sub> permeability is higher than N<sub>2</sub> in all samples due to CO<sub>2</sub>'s temporary quadrupole moment, which enhances its solubility in TPU. The TPU/PLA (20 wt. %) membrane demonstrates competitive gas separation properties (Table 4).

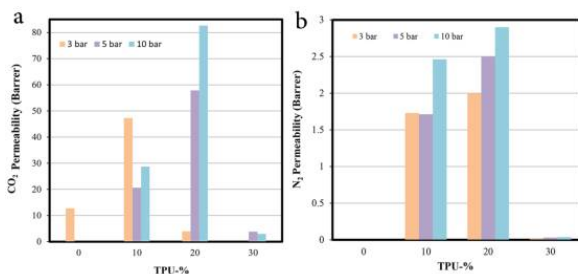


Figure 7. CO<sub>2</sub> and N<sub>2</sub> permeability of the prepared membranes

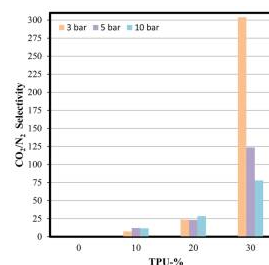


Figure 8. CO<sub>2</sub>/N<sub>2</sub> selectivity of the prepared Membranes

Table 4. The results of the tensile test of the prepared membranes

Membrane	Filler loading (wt%)	P <sub>CO<sub>2</sub></sub> (Barrer)	α <sub>CO<sub>2</sub>/N<sub>2</sub></sub>
TPU/Pebax 1657	60	90	30
TPU/ Cyanuric chloride	10	88	46
TPU/Silica	5	6	42
TPU /CNT@TiO <sub>2</sub>	0.5	68	75
TPU/PLA	20	83	28

#### 5. CONCLUSION

In this study, thermoplastic polyurethane (TPU) was synthesized using PCL 2000, TDI, and BDO in a molar ratio of 4/5/1. PLA (10, 20, and 30 wt. %) was blended with TPU, and membrane films were prepared. FTIR confirmed the chemical structure, while XRD showed a significant decrease in crystallinity at TPU-20%. Gas permeability tests revealed increased permeability and selectivity with higher PLA content.

#### 6. REFERENCES

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