

# EFFECT OF SOYBEAN POLYOL CONTENT ON PHASE SEPARATION OF THERMOPLASTIC POLYURETHANE OBTAINED BY REACTIVE EXTRUSION

Juliano R. Ernzen<sup>1,2</sup>, Angel Marcos-Fernández<sup>3</sup> and Otávio Bianchi<sup>4,2\*</sup>

*1 – Mantoflex poliuretanos, Caxias do Sul, RS, Brazil*

*2 – Programa de Pós-Graduação em Engenharia e Ciência dos Materiais (PGMAT), Universidade de Caxias do Sul (UCS), Caxias do Sul, RS, Brazil*

*3 – Institute of Polymer Science and Technology (ICTP-CSIC), Elastomers Group, Madrid, Spain*

*4 – Department of Materials Engineering (DEMAT), Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil*

**Abstract** – This study aimed to investigate the effect of the partial replacement of polyol polyester with polyol from soybean oil on the structure and properties of thermoplastic polyurethanes (TPUs) produced by reactive extrusion. The results showed that when the amount of soy polyol exceeded 5wt.%, there was an increase in molecular mass and gel formation in TPUs. However, this increase was accompanied by the formation of non-regular structures, which reduced the hydrogen bonding density without affecting the amount of ringed segments dispersed in the flexible ones. Additionally, an increase in the glass transition temperature and a smaller phase separation were observed. These findings can be helpful in the development of PUs with tunable structures.

**Keywords:** Thermoplastics polyurethane, renewable polyol, reactive extrusion.

**Fundings:** OB (grant number 308567/2018-8 and 305814/2021-4). AMF (project PID2020-119047RB-I00).

## Introduction

Segmented thermoplastic polyurethanes (TPUs) are an important class of polyurethanes (PUs) composed of thermodynamically incompatible soft segments (SS), derived from macrodiols, and hard segments (HS), formed by a diisocyanate and a low molecular weight diol (chain extender) [1]. The polarity, solubility parameters ( $\delta_i$ ), and the number of chemical groups capable of hydrogen bonding plays a fundamental role in the microphase separation between the HS and SS segments, affecting the morphology and physicochemical and mechanical properties of the copolymer.

While using renewable sources for PU monomers is not new, the synthesis of TPUs using renewable source polyols remains challenging due to the conversion of soybean oil-based polyols obtained by the epoxidation of double bonds into polyfunctional monomers [2-4]. However, alternative approaches, such as using diacids produced by the Diels–Alder reaction or acids like ricinoleic acid to obtain suitable polyols for TPUs synthesis and partial substitution of petrochemical polyols as adjustments in the reaction process, are being explored [5]. Such approaches produce TPUs with exciting properties, including more excellent hydrolysis resistance than conventional polyesters. In this work, we investigate the synthesis and phase separation of TPUs using reactive extrusion, partially replacing the polyol with a renewable source polyol obtained by the epoxidation of soybean oil.

## Experimental

## Materials

The TPUs were synthesized using 4,4'-diphenylmethane diisocyanate (MDI) purchased from Dow Chemical, Brazil (ISONATE 125M, NCO content = 33.5 wt.%,  $\rho = 1.23 \text{ g.cm}^{-3}$ ) as the isocyanate, and 1,4 butanediol (BDO,  $\rho = 1.02 \text{ g.cm}^{-3}$ ) purchased from Dow Chemical, Brazil as the chain extender. Polyester polyols (Coating YA7220,  $\rho = 1.15 \text{ g.cm}^{-3}$ , the molecular weight of 2000  $\text{g.mol}^{-1}$ , hydroxyl index of 55-60  $\text{mgKOH.g}^{-1}$ ) were procured from Coating, China. A renewable source polyol was also used, which was obtained by epoxidizing soybean oil and had a hydroxyl index of 90  $\text{mgKOH.g}^{-1}$ ,  $\rho = 0.97 \text{ g.cm}^{-3}$ , and molecular weight of 2000  $\text{g.mol}^{-1}$  [2].

## Reactive extrusion

The blends of the renewable polyol with a polyester polyol, ranging from 1 to 50 wt.%, were prepared via mechanical stirring at 80°C for 15 minutes. The pre-polymer was formed in a 5L stainless steel vessel by adding MDI and incorporating the polyol blends. This mixture was maintained at 80°C and stirred during the reactive extrusion process. All TPUs were synthesized with ~50 wt.% HS and a functional groups ratio of 1.05/1 NCO/OH. The pre-polymer and chain extenders were added to maintain a constant production rate of around 2  $\text{kg.h}^{-1}$  of TPU in an LTE 16-48 co-rotating twin-screw extruder (LabTech Engineering Company Ltd., Thailand) with a length-to-diameter ratio (L/D) of 48. The processing temperature range was between 160 to 220°C, and the screw speed was set to 250 rpm. The screw had two mixing sections with kneading elements staggered at 30, 60, and 90°, separated by conveying elements. These processing conditions resulted in an average residence time of roughly 300 seconds. After extrusion, the polymers were cooled in water (25°C) and pelletized for subsequent characterization.

## Size exclusion chromatography (SEC)

The molecular weight of the TPUs was measured through size exclusion chromatography (SEC) using dimethylformamide with 1% of BrLi as an eluent in a Perkin-Elmer series 200 chromatograph equipped with a refraction index detector. The samples were prepared at a concentration of 10  $\text{mg.mL}^{-1}$ , and a flow rate of 1  $\text{mL.min}^{-1}$  was maintained during analysis. The injected volume was 10  $\mu\text{L}$ , and the columns temperature was set at 35°C. Calibration curves were established using polystyrene standards.

## Fourier transform infrared spectroscopy (FTIR)

The chemical structure of the TPUs and the impact of the renewable polyol on phase separation were analyzed using Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer Spectrum 400 spectrometer) in attenuated total reflection mode (ATR) with a diamond crystal positioned at 45°. The samples were scanned 32 times across the range of 4000–450  $\text{cm}^{-1}$ , with a resolution of 2  $\text{cm}^{-1}$ . Additionally, the extent of hydrogen bonding and the dispersion of hard segments within the soft phase were determined via mathematical deconvolution [3, 6].

## Differential scanning calorimetry (DSC)

Differential scanning calorimetry (Mettler Toledo, DSC 822e) was employed to determine the thermal transitions of the polyols and TPUs under a nitrogen atmosphere (50  $\text{mL.min}^{-1}$ ). Samples weighing 9-10 mg were analyzed from -70 to 240°C, with a heating rate of 10  $^{\circ}\text{C.min}^{-1}$ . The  $T_g$  value is reported at the onset point, and the variation of heat capacity ( $\Delta C_p$ ) is calculated at the midpoint ( $\Delta T_g$ ). In addition, model reactions were conducted with MDI-BDO at 80°C, under mechanical stirring, for 1 hour to identify the specific transition temperatures of the rigid phase.

## Results and Discussion

Gel formation was observed in samples containing over 5wt.% soybean oil polyol, rendering it impossible to solubilize the entire sample. Therefore, for samples containing 10wt.% and 20wt.%,

the molecular mass values only apply to the non-gelled fractions. Measurements were not possible for samples containing 50wt.% renewable polyol. For TPU, an  $M_n$  value of 70 kg/mol and  $M_w/M_n$  of 1.74 were observed. When 1wt.% renewable polyol was added, the values remained almost unchanged at 115 kg/mol and 1.76, respectively. However, with 5wt.% renewable polyol, the molar mass increased to 136 kg/mol, and the polydispersity was 2.68. For the soluble fractions of samples containing 10wt.% and 20wt.%, molar masses of 98 kg/mol and  $M_w/M_n$  of 2.2-2.7 were observed. Furthermore, adding 1wt.% soybean oil polyol significantly increased the mass with minimal variation in polydispersity. The increase in  $M_w/M_n$  values directly impacts the flow stability during the reaction, thus making this TPU a promising candidate for extrusion-forming processes [6].

The impact of renewable polyol content was evaluated by analyzing six specific bands in the 1500-1800  $\text{cm}^{-1}$  region, as previously established by studies exploring the relative abundance of hydrogen bonds. Gaussian functions were employed to make mathematical adjustments for each spectrum. These six bands were identified as: (I) 1675  $\text{cm}^{-1}$  for H-bonded urethane carbonyl groups in the ordered phase of hard segments, (II) 1700  $\text{cm}^{-1}$  for H-bonded urethane carbonyl groups in the disordered phase of hard segments, (III) 1710  $\text{cm}^{-1}$  for H-bonded carbonyl groups in the soft-hard segment, (IV) 1728  $\text{cm}^{-1}$  for free carbonyl from urethane groups in the hard segment, (V) 1740  $\text{cm}^{-1}$  for carbonyl-carbonyl interactions in the soft segments, and (VI) 1745  $\text{cm}^{-1}$  for free carbonyl in the soft segment. In addition, the weight fractions of hydrogen-bonded urethane groups ( $X_b$ ), hard segment dispersed in the soft segment ( $W_h$ ), mixed-phase weight fraction (MP), soft phase weight fraction (SP), and hard phase weight fraction (HP) were determined according to literatures [3, 6].

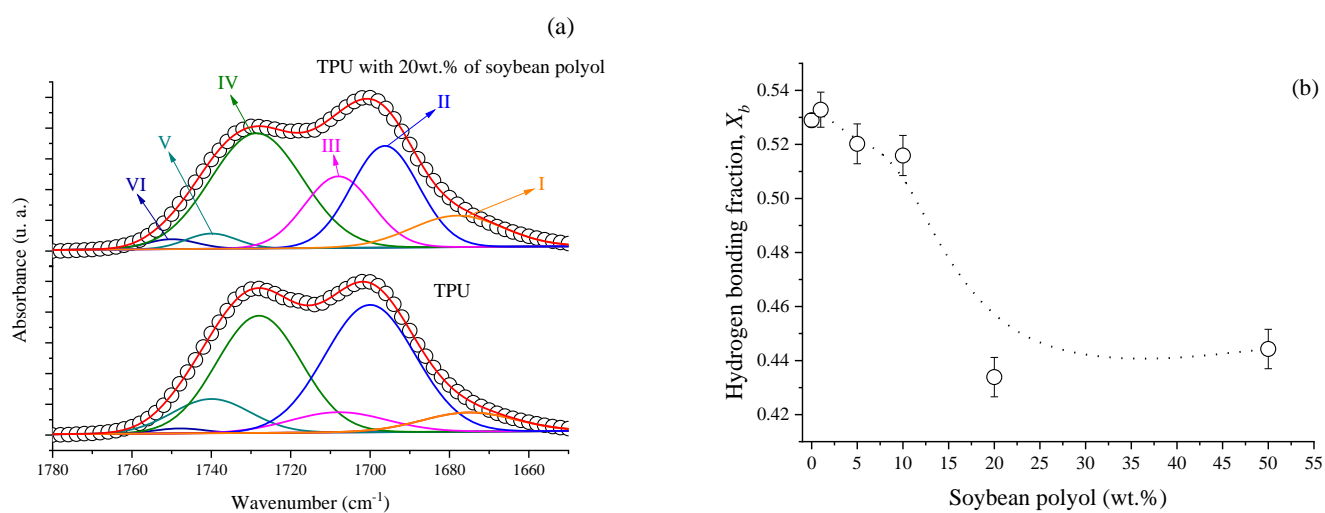


Fig 1. (a) Carbonyl region of the FTIR spectrum corresponding to the 1780-1660  $\text{cm}^{-1}$  was deconvoluted to identify and separate the different molecular components contributing to the signal. (b) The fraction of hydrogen bonding present in the samples.

As anticipated, incorporating a renewable polyol source leads to a decrease in the hydrogen-bonding fraction,  $X_b$ , which reflects the higher concentration of polar groups in the flexible phase. However, it should be noted that there is a relative increase in the band associated with the hydrogen bonds occurring in the flexible phase when soy polyol is increased, as evidenced by the corresponding decrease in the band at 1728  $\text{cm}^{-1}$ . Additionally, the proportion of rigid phase dispersed in the flexible phase remained relatively constant at  $\sim 0.29$ , as did the mixed phase fraction at about  $\sim 0.13$ . The SP values of all TPUs were around 0.68, as were the HP values, which were approximately 0.32.

Adding 5wt.% soy polyol to the TPUs initially caused a reduction in their  $T_g$  from  $-18^\circ\text{C}$  to  $-24^\circ\text{C}$ . This reduction was due to increased free volume and branching in the main chain. However, crosslinks would become evident if more than 5wt.% soy polyol were added due to the polyol's

polyfunctionality. As a result, the  $T_g$  would increase significantly to values up to 82°C with 50 wt% of the polyol. The degree of phase separation (DS) was estimated based on the assumptions of Camberlin and Pascault [7], and the estimated values showed a linear trend ( $DS = -0.72 * polyol (wt. \%) + 77.67$ ,  $R > 0.98$ ). This trend indicated a reduction in phase separation, which was a consequence of the smaller difference in solubility parameters, according to Cruz et al [8].

## Conclusions

The structure of the polyol is a crucial factor that affects the properties and structure of polyurethanes. Generally, the addition of polyol can lead to a reduction in the density of hydrogen bonds, which may result in a decrease in mechanical properties. However, our results showed that adding 1wt.% of polyol increased the molecular weight of the polyurethanes, which resulted in improved rheological stability without forming gels or significant changes in  $T_g$  and phase separation. These findings provide valuable insights into the relationship between the structure and properties of polyurethanes and can guide the development of polyurethane-based materials with optimized properties.

## Acknowledgements

The authors thank the financial support from the Brazilian Agency Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES). OB thanks for National Council for Scientific and Technological Development (CNPq). AMF thanks the Spanish Ministerio de Economía e Innovación for partial financial support.

## References

- 1 . M. Asensio, V. Costa, A. Nohales, O. Bianchi, C.M. Gómez, *Polymers*, 2019, 11, 1910. <https://doi.org/10.3390/polym11121910>.
- 2 . D. Favero, V.R. Marcon, T. Barcellos, C.M. Gómez, M.J. Sanchis, M. Carsí, C.A. Figueroa, O. Bianchi, *Journal of Molecular Liquids*, 2019, 285, 136. <https://doi.org/10.1016/j.molliq.2019.04.078>.
- 3 . D. Favero, V. Marcon, C.A. Figueroa, C.M. Gómez, A. Cros, N. Garro, M.J. Sanchis, M. Carsí, O. Bianchi, *Journal of Applied Polymer Science*, 2021, 138, 50709. <https://doi.org/10.1002/app.50709>.
- 4 . L.N. Dang, S. Le Hoang, M. Malin, J. Weisser, T. Walter, M. Schnabelrauch, J. Seppälä, *European Polymer Journal*, 2016, 81, 129. <https://doi.org/10.1016/j.eurpolymj.2016.05.024>.
- 5 . C. Bueno-Ferrer, E. Hablot, F. Perrin-Sarazin, M.C. Garrigós, A. Jiménez, L. Averous, *Macromolecular Materials and Engineering*, 2012, 297, 777. <https://doi.org/10.1002/mame.201100278>.
- 6 . J.R. Erzen, C.H. Romoaldo, C. Gommès, J.A. Covas, A. Marcos-Fernández, R. Fiorio, O. Bianchi, *Polymers*, 2022, 14, 3164. <https://doi.org/10.3390/polym14153164>.
- 7 . Y. Camberlin, J.P. Pascault, *Journal of Polymer Science: Polymer Chemistry Edition*, 1983, 21, 415. <https://doi.org/10.1002/pol.1983.170210211>.
- 8 . J.A. Cruz, S.C. Amico, O. Bianchi, *Journal of Polymer Research*, 2023, 30, 1. <https://doi.org/10.1007/s10965-022-03393-9>.