PREDICTION OF THERMODYNAMIC BEHAVIOR AND ELASTICITY MODULE FOR THERMOPLASTIC POLYURETHANES BASED ON SOLUBILITY PARAMETER

Lucas P. da Silva[1], Cristofor P.O. da Silva[1], Lucas Dall Agnol[2], Otávio Bianchi[1,2]*

1 – Department of Materials Engineering, Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil
otavio.bianchi@gmail.com
2 – Postgraduate Program in Materials Science and Engineering (PGMAT), University of Caxias do Sul (UCS), Caxias do Sul, RS, Brazil

Abstract In this work, the thermodynamic and mechanical behavior of the thermoplastic polyurethanes (TPU) was described based on the solubility parameter. Two polyester based TPU were used in this study. The phase diagram showed that hard phase percolation occurs at 0.29-0.30, respectively. According to models previsions, as the rigid phase increased, the Young modulus also increased according to the literature [1,2]. The data obtained showed an average percentage difference of less than 5% when compared to experimental data. Through the approaches employed, it was possible to predict the thermodynamic and mechanical behavior of TPUs successfully.
Keywords: *Thermoplastic polyurethane; thermodynamic behavior; Young modulus; solubility parameters.*

Introduction

The TPUs are among the most versatile polymers, playing an increasingly important role in the industry. A wide spectrum of tailor-made properties can be obtained by modifying their formulations, which are generally composed of hard and soft segments based on isocyanates (–NCO), polyols (-OH), and chain extenders. Polyols form the soft segment (SS), responsible for rubber-like characteristics and elasticity of the elastomers. The hard segment (HS) is formed by the reaction with the isocyanate and short-chain diols employed as chain extenders that affect the mechanical features, like hardness, elasticity, and tearing strength [3]. As a result of the thermodynamic incompatibility between the segments, TPUs suffer phase segregation. This segregative behavior has been the subject of studies since the mid-1960s, when it was proposed that the segregation of HS forms domains that impact the polymer's mechanical properties [4].

The segmented morphology of TPUs depends on the physicochemical characteristics of the segments. The molecular mass, chemical composition, molecular architecture, and processing conditions can induce a percolation-type transition between domains. When percolating, HS domains can form different types of structures: spheres, cylinders, and lamellae that depend on interactions and fraction of the segments. However, determining the percolation limit based on system formulation variations is very complex. Considering that morphology impacts the mechanical properties of TPUs, many approaches have been employed to determine how to correlate the morphological characteristics of the copolymer with the mechanical properties [1].

Based on micromechanical assumptions, Ginzburg *et al*. [2] performed the prediction of Young modulus of the TPUs containing HS of diphenylmethane diisocyanate with butanediol or diethyltoluenediamine (MDI-BDO and MDI-DETDA) and as a SS of poly(propylene oxide) (PO). They also addressed toluene diisocyanate, TDI-based multifunctional TPU networks. The Young modulus was estimated using a combination of thermodynamic models, rubber elasticity theory, and

an approach proposed by Kolarik [5], who used an 'equivalent box model' (EBM) to predict the mechanical behavior and, also used to predict the diffusion of polymeric blends. Regarding thermodynamic considerations, the use of solubility parameters was used to describe the phase separation of TPUs [2]. Although the approach presented by the authors is of great importance, in the study no data is showing its effectiveness using solubility parameters for polyester-based TPUs.

Polyester polyols are used as SS in TPUs. It is known that these polyols usually result in TPUs with the high elastic modulus (50–1000 MPa) due to the large relative fraction of hydrogen bonds. Yet polyols such as polycaprolactone (PCL) can be biodegradable and used in a wide range of applications [6]. In the present work, concepts based on solubility parameters were used to predict the thermodynamic behavior and elasticity of TPUs. The approach was carried out using solubility parameters estimated by groups contribution in real TPU formulations. Comparisons between theoretical and experimental results were carried out in order to validate the methodology addressed to aid in the future synthesis of TPUs with tunable properties.

Theoretical background

The cohesive energy (E_{coh}) of a substance in a condensed state is defined as the increase in internal energy (U) by mole of substance if all the intermolecular forces are eliminated [7]. Thus, we can relate E_{coh} to the solubility parameter (δ) by Eq. 1:

$$\delta = (\frac{Ecoh}{V_m})^{1/2} \tag{1}$$

In 1953, Small [7] demonstrated that the solubility parameter could be described by the Eq. 2:

$$\delta = \frac{F}{V_m} \tag{2}$$

Where V_m is the molar volume and F is the molar constant of attraction defined by $F = (E_{coh}/V_m)^{1/2}$. Van Krevelen established F values for certain chemical groups, this allowed us to estimate the solubility parameter using group theory from the cohesive energy for polymers [7].

Determination of the Incompatibility Parameter

In this work, for simplification, we neglected the polydispersity of the segments. Considering that the SS has functionality equal to 2, we can define the equivalent weight of the SS as: $E_s = M_s/f_p$, in which M_s is the molecular mass and f_p is the functionality. As such, the numerical average molecular weight of HS can be described by the following relationship with the weight fraction of HS (f):

$$M_H = 2E_S \frac{f}{1-f} \tag{3}$$

After determining the molecular weight variables, the incompatibility parameter (χ_N) can be obtained, according to Eq. 4, by the product of the Flory-Huggins parameter, χ, (Eq. 5) with the chain lengths of each segment (N_H and N_s), described in Eq. 6 and 7:

$$\chi_N = \chi[N_H + N_S] = \frac{(\delta_h - \delta_s)^2}{RT}[\frac{M_H}{2\rho_H} + \frac{E_S}{\rho_S}] \tag{4}$$

$$\chi = \frac{v_{ref}(\delta_h - \delta_s)^2}{RT} \tag{5}$$

$$N_H = \frac{M_H}{2(\rho_H v_{ref})} \qquad \text{and} \qquad N_S = \frac{E_S}{(\rho_S v_{ref})} \qquad (6\text{–}7)$$

Where, δ_h and δ_s ate the solubility parameter for HS and SS, respectively. Both calculated by the Van krevelen method [7], ρ_H and ρ_s are the densities of HS and SS, respectively. V_{ref} is the reference volume is the same as V_m of each SS.

For analysis of the morphology in the systems, the incompatibility parameter was used in a phase diagram allowing to define of the conformation of the formed domains. The diagram is estimated by Eq. 8 [2]:

$$(\chi N) = (\chi N)_0 \frac{1}{1 - \dfrac{0,25 - f(1-f)}{0,25 - \alpha_i}} \qquad (8)$$

Where $(\chi N)_0$ is the pre-factor coming from the fluctuation theory for multiblock copolymers (ranging from 15–20 depending on the number of blocks and stipulated by average approximation as 15 in this study), and α_i is the order-disorder constant for each transition. Assuming the values of α_1 (disorder-sphere) = 0, α_2 (sphere-cylinder) = 0.098, α_3 (cylinder-lamella) = 0.206.

Micromechanical Model

Considering that the modulus can be described by an EBM-type equation, the elastomer modulus is given by Eq. 9 [5]:

$$E(f) = vpE_H + (1 - vp)E_{FS} \qquad (9)$$

Where E_H is the modulus of the HS. In this study, was estimated by group contribution having a value of 2346 MPa for phenylene diisocyanate with butanediol (PPDI-BDO) and 5425 MPa for diphenylmethane diisocyanate with butanediol (MDI-BDO). It also considered that the volume of the elastically active fraction of the percolated HS (v_p) is given by Eq. 10:

$$v_p = \left[\frac{f - f_{perc}}{1 - f_{perc}}\right]^\gamma \qquad (10)$$

Here, γ is the experimental percolation exponent (values could be larger than 2) [8, 9]. Therefore, the contribution of the rigid segment and the loaded flexible segment (E_{FS}) is calculated. When $f=f_{SC}$, the hard phase spheres aggregate into infinite cylinders, the percolated hard phase is formed. The "soft phase filled" consists of the soft phase matrix and the hard phase spheres. The modulus increase provided by the spheres can be estimated by Eq. 11[10]: This assumption is a crucial link that relates thermodynamic information about the HS (its cohesive energy density or solubility parameter) to the mechanical properties of HS-based TPUs.

$$E_{FS} = E_{SP} + (2.5X)E_{SP} \qquad (11)$$

Where E_{SP} is the pure SS modulus coupled with the modulus of the flexible matrix loaded with rigid phase spheres represented by the factor in the parentheses whose X ranges from 0 when $f < f_{DS}$ to $f - v_P - f_{DS}$ when $f > f_{DS}$. The modulus of the pure SS (network elasticity model) E_S is defined by Eq.12:

$$Es = \frac{3\rho RT}{Mx}\left(1 - \frac{2}{f_p}\right) + \frac{3\rho RT}{Mc} \qquad (12)$$

Where R is the gas constant, M_x is the molecular weight between crosslinks in the network, M_c is the critical molecular weight, and T is the absolute temperature.

Experimental

Materials

TPU formulations with different HS and SS were utilized. For a first comparison, denominated TPU1, we used the data published by [1], which in the polymers presented there is a HS variation between 11–27 wt.%. This system is formed by PPDI and BDO, the SS formed by PCL, with a molar mass 114g/mol. The other TPU (TPU2) was supplied by the company Mantoflex (Brazil), it is a polyester with formulation: 4,4'-diphenylmethane diisocyanate (MDI), BDO and SS (polyol blend 20:40:40 wt.%; PET; M_w = 192 g/mol), PBA; M_w= 216 g/mol and PEA; M_w = 188 g/mol).

Results and Discussion

The solubility parameters obtained for HS for each system showed distinct values, with (PPDI-BDO; ρ=1.17 g/mol) at 25.59 $(J/cm^3)^{1/2}$, while (MDI-BDO; ρ=1.27 g/mol) showed a value of 26.57 $(J/cm^3)^{1/2}$. The δ_s values for TPU1 were 19.10 $(J/cm^3)^{1/2}$ and 18.63 $(J/cm^3)^{1/2}$ for the TPU2. These values were generated according to the group contributions following Van Krevelen's approach [7]. The results found are in agreement with the literature [1, 7, 11].

In Fig. 1 two thermodynamic diagrams for the two TPU systems are shown. For both systems, the χ_N displayed similar behavior. In both systems, it is assumed that when the hard segment weight fraction crosses the S-C line it can be associated with the onset of percolated hard phase. If the hard segment weight fraction (f) is below the D-S line, we can expect that all the hard segments are mixed with the flexible segments, and the polymer is homogeneous.

As f increases, the individual rigid segments become longer and more prone to aggregation. Then, after the line intersects the D-S line, the polymer morphology is such that islands of HS domains are dispersed evenly in the flexible phase matrix. As the line crosses the S-C line, the hard phase domains transition to long fibers and then, at the C-L line, to lamellae. In practice, between these two points is the "percolation threshold," f_{perc}. Below percolation, the hard phase domains contribute very little to the elastomer hardness, but above percolation, they increase the modulus very significantly, as shown in the Young modulus results (Fig. 2).
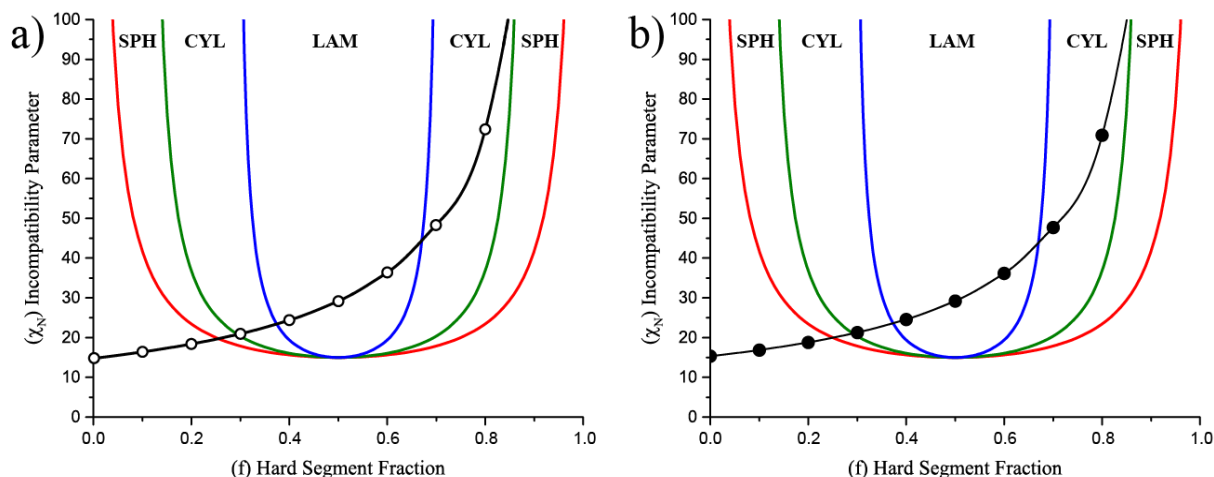

Figure 1 – Phase diagram for block copolymers in the analyzed systems. The red curve symbolizes the transition in the disorder-sphere system, while the blue curve represents the change sphere-cylinder and subsequently to lamellae in the green curve. The black curves show the behavior of χN as a function of HS weight fraction for: (a) TPU1 (line-square) and (b) TPU2 (line-circle)

For TPU1 [Fig. 2(a)], the found values showed an agreement with the literature [1]. Although TPU systems with PCL increase their fraction of hydrogen bonds with the amount of HS, the proposed

model predicted the experimental data with an average percentage difference of 4.5%. For TPU 2 [(Fig.2 (b)] a good agreement with the experimental data was also noted, having a difference of 1.4.
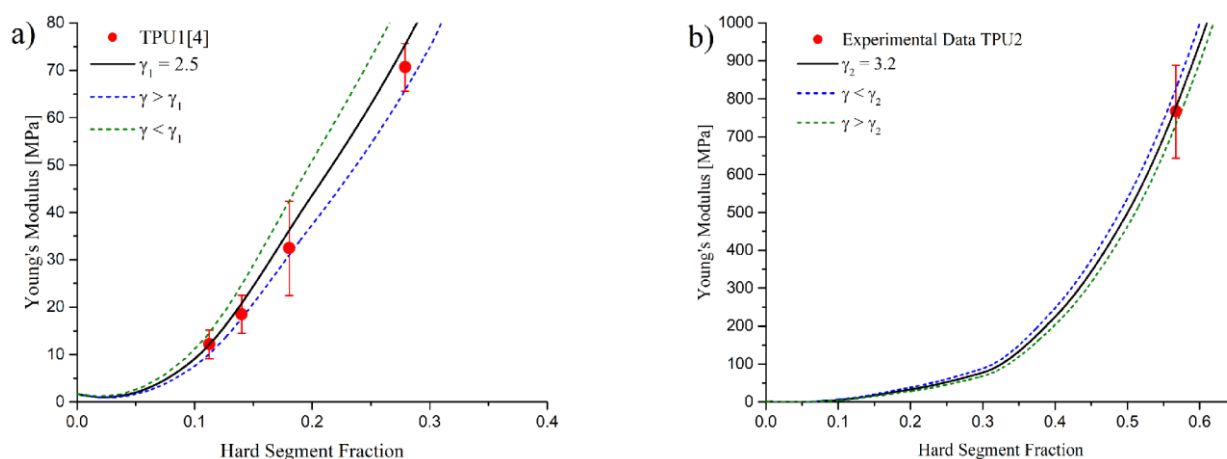

Figure 2 – Young's modulus as a function of the HS fraction: (a) TPU1 with percolation exponent, $\gamma = 2.55$, $f_{perc} = 0.29$, and (b) TPU2 with percolation exponent, $\gamma = 2.90$ and $f_{perc} = 0.30$

Conclusions

The dependency of the mechanical properties by TPUs using polyester as a SS can be explained qualitatively using a combined thermodynamic-micromechanical model. The approach used successfully predicts several observed trends, such as an increase in Young's modulus with HS weight fraction and higher modulus values for higher cohesive energy density systems.

Acknowledgements

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