Bio-based Thermoplastic Polyhydroxyurethanes Synthesized from the Terpolymerization of a Dicarbonate and Two Diamines: Design, Rheology, and Application in Melt Blending

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ABSTRACT

The terpolymerization of bio-based diglycerol dicarbonate (DGC) and Priamine 1074 is conducted with aminopropyl terminated polydimethylsiloxane ($M_n = 1,000$ g/mol, PDMS) or 1,10-diaminodecane (DAD). Depending on DGC contents and PDMS/Priamine 1074 ratios, the resulting amorphous thermoplastic polyhydroxyurethanes (TPHUs) present random or block copolymer-like segmented structures. These TPHUs exhibit nanophase separation of small interdomain spacing (3-3.5 nm), mainly caused by DGC. As for DAD, it introduces crystallinity (8%) and chain ordering into the TPHU structure, as observed from X-ray measurements. Some PDMS-based TPHUs are blended with PLA, and the blends are found to be partially miscible as they exhibit two T_gs, and their estimated relative energy differences (RED), calculated from Hoftyzer-Van Krevelen's group contribution method, are nearly unity. Based on the type of hydrogen bonding interactions and the extent of immiscibility (RED) of each of the blends, the TPHUs find potential applications as rubber tougheners and/or plasticizers for PLA.

INTRODUCTION

Non-isocyanate polyurethanes (NIPUs) have been a subject of interest of many researchers, particularly in the last decade, because they are prepared without isocyanates, a dangerous and lethal main component of conventional polyurethanes (PUs).^{1, 2} The polyaddition of cyclic (poly)carbonates with (poly)amines constitutes one pathway that leads to NIPUs with pendent hydroxyl groups in their chains, known as polyhydroxyurethanes (PHUs). PHUs are prominent materials because their polymerization does not lead to lower molecular weight byproducts and their precursors are abundant and, most importantly, can be derived from bio-based and biorenewables sources. ²⁻⁴ Indeed, cyclic carbonates were previously synthesized from vegetable oils, bio-polyols (sugars) and terpenes. ⁵⁻⁷ Some of these natural materials contain double bonds which are first epoxidized and then carbonated through the chemical fixation of carbon dioxide.⁸ Bio-based diamines have been also synthesized from plant-based fatty acids, and some of them are commercially available, such as the Priamine family from Croda.⁹⁻¹¹ Hence, the synthesis of bio-based PHUs complies with many different green chemistry principles; the elimination of hazardous materials, such as isocyanates, the substitution of non-renewable fossil-fuels with renewable feedstocks, the reduction of organic solvent usages as reactions can be conducted in bulk, and the reduction of wastes and byproducts since the polyadditions do not generate lower molecular weight byproducts.¹²

An interesting renewable source for making the cyclic carbonates is diglycerol. Diglycerol dicarbonate (DGC), explored extensively in the literature for different PHU formulations, ¹³⁻²⁵ is derived from glycerol, which is a byproduct obtained from the hydrolysis of biomass wastes, the methanolysis of triglycerides, and the production of biodiesel. ⁴ The worldwide annual production of glycerol has drastically increased in the past decade, and predictions showed that

the production of glycerol was 6 times higher than the demand in 2020, making it an abundant raw material for the synthesis of PHUs. ^{4, 26} Furthermore, DGC has a melting point around 65 °C, ^{13, 14} so bulk polyadditions are possible at moderate temperatures.

In this study, DGC (hard segment) is combined with Priamine 1074, a bio-based diamine derived from dimer fatty acids (base of the soft segment). The reaction between DGC and Priamine 1074 leads to rubbery yellowish PHUs, as indicated previously, ^{14, 22} so this work seeks the preparation of a new family of thermoplastic PHUs (TPHUs) based on these monomers while further altering the polymer with a second diamine added to form a terpolymer. Two different diamines are considered; the aminopropyl terminated polydimethylsiloxane with $M_n = 1,000$ g/mol (PDMS-1k-(NH₂)₂), which is softer than Priamine 1074, and 1,10-diaminodecane (DAD), which is derived from castor bean oil ¹¹ and enhances crystallinity more than Priamine 1074. While bio-based TPHUs have been extensively studied in the literature, ²⁷⁻³⁴ a similar strategy was adopted by few, ^{23, 34} mainly, those done by Mülhaupt et al. where thermoplastic and thermoset PHUs were prepared by blending two di/tricarbonates together or two diamines to tune the properties of their bio-based materials. ^{27, 35, 36}

However, blending more than one diamine draws a question about the nanophase separation and the rheological behavior of the final TPHUs. Like conventional thermoplastic polyurethanes (TPUs), the reaction between the hard segments (dicarbonates) and the soft segments (diamines) produces segmented di/triblock copolymer TPHUs whose microstructure and rheology might deviate from those of standard homopolymers. ³⁷⁻⁴³ Beniah et al. explored in depth the formation of nanophase separation in their segmented PHUs, notably in those prepared from poly(tetramethylene oxide)-based diamines. In their studies, the authors investigated the effects that the choice of the dicarbonates, diamines, and chain extenders as well as the functionalization of the hydroxyl groups have on tuning the nanophase separations of their TPHUs. ⁴⁴⁻⁴⁹ Nevertheless, there have been limited findings on the rheological behavior of such systems and their compliance to previously established models used for conventional polymers. Hence, this article tries to address these aspects, which should be especially interesting as PHUs exhibit additional hydrogen bonding interactions due to the presence of hydroxyl groups. ^{10, 44-49}

Moreover and to the best of our knowledge, TPHU blends with other polymers, such as poly(lactic acid) PLA, have not been studied. PLA is a well-known bio-based and biodegradable polymer with outstanding physical and mechanical properties, but it suffers from poor ductility and impact toughness. Therefore, many TPUs were extruded with PLA with the intention to plasticize the latter and increase its toughness and ductility. ⁵⁰⁻⁶² Hyperbranched poly(ester amide) with a high hydroxyl functionality were also blended with PLA, and the authors found that the additive was partially miscible with the polymer matrix at high concentrations (20 wt.%). ⁶³ Like these poly(ester amides), our TPHUs will have hydroxyl groups available for compatibilization and may provide some miscibility with the PLA matrix.

This study starts by examining the effects of mixing Priamine 1074 with PDMS-1k-(NH₂)₂ or DAD in combination with DGC. The resulting TPHU's structural, thermal, rheological, and mechanical properties are studied with varying the DGC/Primaine 1074/second diamine ratios. Then, the blends of PLA with some of the TPHUs are prepared and characterized, and the application of the TPHUs as the dispersed phase is assessed.

MATERIALS AND METHODS

Materials

Diglycerol (DIG, $\geq 80\%$ α, α , impurities consist of mono-, α, β -di-, β, β -di, and triglycerol) was obtained from Tokyo Chemical Industry (TCI). Dimethyl carbonate (DMC, ≥99%, anhydrous) and potassium carbonate (K₂CO₃, 98%, anhydrous powder) were purchased from Acros. Ethyl acetate (EthOAc, certified grade), tetrahydrofuran (THF, HPCL grade), chloroform (stabilized with ethanol), heptane, and 1,4-dioxane were purchased from Fischer Chemical. Water purified by a reverse osmosis process was provided by the McGill Chemical Engineering Department. Priamine The diamines used in this work are 1074. aminopropyl terminated polydimethylsiloxane with $M_n = 1,000$ g/mol (PDMS-1k-(NH₂)₂), and 1,10-diaminodecane (DAD) which were provided by Croda, Gelest, and Sigma Aldrich, respectively. Deuterated dimethyl sulfoxide (DMSO-d₆) and chloroform (CDCl₃) was purchased from Sigma Aldrich. Poly(lactic acid) (PLA) was purchased from NatureWorks, Product ID Ingeo[™] Biopolymer 2003D. All the chemicals were used as received. Only PLA was dried overnight under vacuum at 40 °C before the extrusion to remove any adsorbed moisture.

Experimental methods

DGC synthesis and purification: The synthesis and purification of DGC were conducted following the procedure detailed in previous studies on DGC-based hybrid PHUs. ²² The DGC yield was 58%, based on the total amount of DIG originally loaded. The labelled ¹H-NMR spectrum of DGC is given as Figure S1.

Thermoplastic PHU (TPHU) synthesis: The PHU terpolymers were synthesized using a onestep bulk polyaddition method with systematic alteration of the proportion of Priamine 1074 with either PDMS-1k-(NH₂)₂ or DAD. The TPHUs were prepared by adding DGC, Priamine 1074, and one of the diamines to a 50 mL three-neck reactor. After adding a high viscosity stir bar into the mixture, the contents were purged with nitrogen for 15 min before immersing the reactor in an oil bath pre-heated to 80 °C. The reaction was allowed to proceed for 24 h, after which the reactor was removed from the oil bath to cool down and the TPHU was collected. The remaining monomers were removed by dissolving the TPHUs in chloroform and filtering them to remove the undissolved DGC. Then, a 10-fold excess of heptane was added to precipitate the polymers while removing the unreacted diamines and DGC. All terpolymers investigated herein have a hard segment content ranging between 25 and 55 wt.%. The ratio of Priamine 1074 to either PDMS-1k-(NH₂)₂ or DAD was varied from 60/40 to 100/0 (wt.%). In subsequent discussions, these terpolymers are referred to as PDMS-2040 or DAD-2040, for example, where PDMS or DAD written before the dash refers to the second diamine used, the first two digits represent the content of these diamines in the soft segment mixture (in wt.% with respect to Priamine 1074) and the last two (40 in this case) represent the hard segment (DGC) content (in wt.%). Different hard to soft segments concentrations were considered herein to make TPHUs of equimolar ratios and excess of hard segment.

Extrusion: PLA was blended with different PDMS-based TPHUs using a conical intermeshing twin-screw extruder (Haake Minilab, Thermo Electron Corporation, Beverly, MA, USA) with a screw diameter of 5/14 mm in the conical section, a screw length of 109.5 mm, and two batches equal to 3 g each. A three-step process was used to ensure homogeneity of the blends. In the first step, PLA was combined with 20 wt.% TPHU to make a batch of 3 g, and the extruder was set at 150 °C with a screw rotation speed of 30 min⁻¹, and the resulting blend was recycled through the extruder with an additional 1.5 g of the mixture for a second step and then

for a third one to ensure that the polymers were well mixed. The concentration of 20 wt.% was chosen to reflect a typical amount of plasticizer or impact modifier that is used industrially.

Characterization methods

Proton nuclear magnetic resonance (¹H-NMR) spectroscopy: Solution-phase NMR spectra were recorded on a Brucker 500 MHz instrument (16 scans) at ambient temperature. DGC was dissolved in DMSO-d₆, whereas the TPHUs were dissolved in CDCl₃ to be analyzed.

Fourier transform infrared (FTIR) spectroscopy: FTIR measurements were carried out on a Perkin Elmer instrument (Spectrum II series) equipped with a single bounce diamond attenuated transmission reflectance (ATR) for solids and zinc selenide (ZnSe) holder for liquids. 32 scans were recorded for each sample over the range 4000-500 cm⁻¹ with a normal resolution of 4 cm⁻¹. The TPHUs were measured as is, whereas the blends were solvent cast from 1,4-dioxane.

Size exclusion chromatography (SEC): The TPHUs molecular weight distributions were analyzed via SEC. Number average molecular weight (M_n) and dispersity ($D = M_w/M_n$) of prepolymer samples were measured using this technique on a Waters Breeze instrument with HPLC grade THF as an eluent at a flow rate of 0.3 mL/min. The GPC has three Waters Styragel HR columns (HR1 with a molecular weight measurement range of 10^2 to 5×10^3 g/mol, HR2 with a molecular weight measurement range of 5×10^2 to 2×10^4 g/mol, and HR4 with a molecular weight measurement range of 5×10^3 to 6×10^5 g/mol), a guard column, and a refractive index (RI 2414) detector. The columns were heated to 40 °C during analysis. The molecular weights were determined relative to poly(methylmethacrylate) (PMMA) calibration standards from Varian Inc. (ranging from 875 to 1,677,000 g/mol). The reported molecular weights were all relative to the PMMA standards and not adjusted with Mark-Houwink parameters.

Thermogravimetric analysis (TGA): TGA was performed on a Q500 system from TA Instruments. The thermal degradation of the synthesized PTHU was measured at a heating rate of 20 °C/min over the temperature range of 25 to 600 °C under a nitrogen atmosphere. The 10% degradation temperature ($T_{d,10\%}$) were calculated using this method.

Differential scanning calorimetry (DSC): DSC was performed using a Q2500 TA Instruments calorimeter autosampler employing standard hermetic aluminum pans, calibrated with indium and nitrogen as purge gas. The instrument is equipped with a cooling unit allowing it to reach low temperatures up to -90 °C. The samples were analyzed at a heating rate of 10 °C/min, for the second heating ramp, over a temperature range of -90 °C to 100 °C (DAD TPHUs) or 150 °C (PDMS TPHUs and extruded PLA samples) under a nitrogen atmosphere after quenching the samples. Glass transition temperatures (T_g), crystallization temperatures (T_c), melting points (T_m), and the associated enthalpies with the crystallization and the melting (Δ H_c and Δ H_m, respectively) were calculated from the second heating ramp.

Small and Wide Angle X-ray Scattering (SAXS and WAXS): SAXS and WAXS spectroscopy measurements were recorded on a SAXSpoint 2.0 (Anton Paar, Austria) equipped with a CuK α radiation source (wavelength, $\lambda = 1.54$ Å), using a detector of Eiger R 1M (Horizontal) at SAXS and WAXS distances of 1075.9 and 113.1 mm, respectively. The TPHU samples, with thickness of 1 mm, were placed on a sample holder for solids (10 by 10 mm) provided by Anton Paar, which was further secured by tape. X-ray exposure times were 30 min per frame for a total of 4 frames for every experiment. The obtained SAXS profiles were corrected and shown as function of scattering vector ($q = (4\pi/\lambda) \sin\theta$, where 2θ is the scattering angle in $^{\circ}$ and q in nm⁻¹). The mean interdomain spacing, d (nm), was calculated from the obtained SAXS spectra using the following formula:

$$d = \frac{2\pi}{q_{max}}$$
 Eq. (1)

with q_{max} (nm⁻¹) is the value of q at maximum peak position read from SAXS spectra.

Rheology: For all rheology tests, TPHU samples containing PDMS-1k-(NH₂)₂ were cut into disks of 25 mm diameter and a thickness of 1 mm. Those samples were flexible at room temperature, so no hot pressing was required. The samples containing DAD and the blends had to be hot pressed between Teflon plates using a mold to make bars with dimensions of 50 mm length (length cut to 45 mm when running the tests), 10 mm width, 1 mm thickness, and 36 mm gauge length. Pressing was performed at 80 °C for the DAD TPHUs and 150 °C for the blends using three cycles of 5, 10, and 15 metric tons for 10 min each.

Amplitude and frequency sweep measurements were conducted on the TPHU samples using different configurations on an Anton Paar Instruments rheometer (MCR 302). The parallel plates of 25 mm diameter (PP 25) configuration (gap of 1 mm) used with the samples containing PDMS-1k-(NH₂)₂, whereas the torsion configuration (SRF 12) was used with the DAD-containing samples. Amplitude sweep measurements were all conducted at room temperature (~22 °C). The PDMS containing TPHUs were measured at a frequency of 10 Hz and a shear strain ranging from 0.01% to 100%. The DAD containing TPHUs measurements were done at shear strains ranging from 0.001% to 0.1% and a frequency of 10 Hz. Frequency sweeps were conducted at different temperatures, under nitrogen and using a CTD 450 convection oven, starting from room temperature (~25 °C) then 30 °C, after which the temperature was increased at 10 °C increments. All the samples were stabilized at a given temperature for 10 min before running a given test. The 10 min count started after the rheometer had reached the desired

temperature. The PDMS containing TPHU samples were measured at a shear strain of 0.5%, frequency range of 0.1 to 100 rad/s, and temperatures of 25 to 120 °C.

Dynamic thermal mechanical analysis was conducted on the blends. Samples were loaded in tension and a temperature ramp was performed from 25 °C to 150 °C at a rate of 5 °C/min, with an oscillation strain of 0.5% and a frequency of 1 Hz. Amplitude and frequency sweeps were also performed on the blends in the form of bars and disks at room temperature (~22 °C) and 150 °C, respectively, with shear strains and frequency varying depending on the test and the temperature used. For all of the frequency sweeps tests conducted in this study, assurance that the experiments were operating in the viscoelastic region was conducted by performing amplitude sweeps on the samples.

Mechanical Testing: Tensile properties were determined at ambient temperature using an EZ Test (Shimadzu) tensile machine at speeds of 10 mm/min, on the DAD-containing TPHUs, and 20 mm/min, on films of the blends, with a load capacity of 10,000 N. Young's modulus (E), tensile strength (σ_{max}), and elongation at break (EB %) were estimated by the average of at least three repeated samples. Free-standing dog-bone-shaped TPHU samples were prepared using Teflon plates with molds of the following dimensions: length of 50 mm, width of 3 mm, thickness of 1 mm, and gauge length of 25 mm. Pressing was performed at 80 °C using three cycles of 5, 10, and 15 metric tons for 10 min each.

The extruded blends in contrast were solvent-cast using chloroform. 2.5 g of the samples were dissolved in 25 mL of chloroform and then poured into dishes of 12 cm diameter. The dishes were covered with aluminum foil perforated from four different sides to allow chloroform to evaporate slowly. After three days, the films were cut (60 mm length, gauge length of 30 mm, 10 mm width, and thickness between 0.1 and 0.2 mm). The films were dried in a vacuum oven

overnight at 40 °C before running the tests. Similar film preparation methods were adopted elsewhere. ⁶⁴ The tensile properties were monitored on WinAGS Lite software.

Scanning Electron Microscopy (SEM): The morphology of the prepared blends was studied with a Hitachi SU-3500 Variable Pressure SEM. The samples were immersed in liquid nitrogen for 10 min before brittle fracture. A series of samples had their surface directly treated with THF for 5 min to dissolve the TPHUs while keeping the PLA matrix, to provide contrast between the two components. Note that PLA has a low solubility in THF at cold temperatures, enabling its resistance to etching. ⁶⁵ The fractured surfaces of all samples (treated and untreated) were tested after spraying them with palladium.

RESULTS AND DISCUSSION

Characterization of the PDMS containing TPHUs

The polyaddition of DGC and Priamine 1074 was previously studied, and at similar reaction conditions to the ones used herein (80 °C for 24 h), the conversion of the cyclic carbonates is expected to be incomplete. ¹⁴ This was confirmed by performing FTIR on the TPHUs before and after purification and examining the decrease in the area of the carbonyl stretch related to the cyclic carbonate end-groups and unreacted carbonates (at 1780 cm⁻¹) with respect to that of the carbonyl stretch of the urethane linkages (at 1695 cm⁻¹) (Figure S2). The TPHUs prepared from 40 wt.% hard segment content have an excess of cyclic carbonates (60-66 mol.%), whereas the ones containing 25 wt.% have a reaction mixture close to equimolar ratios (45-50 mol.% of hard segments). Hence, the amount of remaining DGC was higher in the former systems (25-35%) than in the latter (2-15%); however, after taking into consideration the diamine content participating in the reaction, the effective amount of unreacted DGC is found to be between 4

and 7%, which complies with the values reported for the equimolar systems. Besides, Carré et al. calculated a 12% residual of their dicarbonate after reacting it with Priamine 1075 at similar conditions to this study. ³⁴ These results were confirmed by conducting ¹H-NMR on the TPHUs (Figure S3, Figure S4, and Table S1) which also showed that the polyadditions with PDMS-1k-(NH₂)₂ decreased the amount of secondary hydroxyl groups with respect to primary hydroxyl groups in the TPHU chains (please see Section II - ¹H-NMR of the Supporting Information for more details on the analysis). The PDMS containing TPHUs are denoted in future discussions according to the following: PDMS-XXYY with XX represents the PDMS weight percentage in the total diamine mixture while YY represents the DGC weight percentage. For example, PDMS-2040 means that the TPHU based on DGC and Priamine 1074 is prepared from 20 wt.% PDMS-1k-(NH₂)₂ in its soft segment mixture and 40 wt.% hard segments (DGC).

The structural and thermal properties of the TPHUs discussed in this section are summarized in **Table 1**. Depending on the hard segment content, whether it is 25 or 40 wt.%, the SEC, DSC, and TGA traces showed interesting differences. The number average molecular weights (M_n) and the dispersity (D) of the PDMS-XX40 TPHUs were similar, with the molecular weight distribution becoming slightly broader when using 40 wt.% PDMS in the soft segment mixture (PDMS-4040). The thermal stability of these TPHUs was also similar with the degradation temperatures matching and with little difference (Figure S5). Nevertheless, the DSC traces showed two glass transitions (T_gs); one at -30 °C indicating the presence of PDMS soft segments and another one at -14 °C indicating the presence of Priamine 1074 soft segments. The first T_g was associated with PDMS segments as a PDMS-10040 TPHU was prepared, and it revealed a T_g at -35 °C. The existence of two T_gs suggests that PDMS-2040 and PDMS-4040 present segmented blocky structures with DGC joining the different soft segments. The soft segments

might have reacted with DGC (in excess) first, which leads to two different PHUs, and then DGC bridged between one Priamine 1074 segment from one chain and another PDMS segment from a second chain by reacting with their free amines. Since the PDMS-XX25 TPHUs presented one Tg, the only factor that could be responsible of having two Tgs in the PDMS-XX40 TPHUs is the excess of DGC, which might have given more cyclic carbonate sites for the soft segments to react separately before they were joined by a cyclic carbonate group. Besides, these TPHUs showed interdomain spacings (d) between their segments (DGC, PDMS-1k-(NH_2)₂, and Priamine 1074) of 3.2 to 3.4 nm which proves that such the TPHUs exhibit nanophase separation. However, this separation is mainly between DGC and Priamine 1074, as d slightly increases with the amount of PDMS, and d are much lower than previously measured ones in Beniah et al.'s segmented PHUs (~10 nm). 44-49 Hence, the soft segments of the TPHUs have a good miscibility with each other (Priamine 1074 and PDMS-1k-(NH₂)₂) and the hard segment (DGC) is inducing the phase separation. Although we are not totally dismissing that the observed two T_gs are caused by the presence of a mixture of two different PHU chains, it is most probable that PDMS-2040 and PDMS-4040 are made of segmented "block copolymers" of two PHUs (Priamine 1074 and PDMS-1k-(NH₂)₂-based) connected by a DGC unit because, the soft segments are miscible and, otherwise, the SEC traces would have been bimodal rather than monomodal, and the M_n and \tilde{D} would have been higher than the values reported in Table 1, especially that an M_n of 15,200 g/mol was measured for a PDMS-10040 TPHU (versus 5,800 g/mol for PDMS-0040) under similar SEC experimental conditions. Figure 1-A illustrates the segmentalization discussed in this last section.

To further prove that the soft segments are miscible and explain the observed two T_{gs} of the PDMS-XX40 TPHUs, a group contribution method, based on Hoftyzer-Van Krevelen, was

conducted to estimate the Hansen solubility parameters of Priamine 1074/DGC and PDMS-1k-(NH₂)₂/DGC hydroxyurethane linkages. ⁶⁶⁻⁶⁸ In general, for liquids and amorphous polymers, the cohesive forces are dependent on the dispersion forces, polar forces, and hydrogen bonding, and hence the solubility parameter estimation is divided into three components; δ_d , δ_p , and δ_h , respectively. ⁶⁶ The estimations, summarized in Table S2, showed that the difference in solubility parameters ($\Delta\delta$), calculated from Eq. (S.8), of Priamine 1074/DGC and PDMS-1k-(NH₂)₂/DGC hydroxyurethane linkages is about 5.2 (MJ/m³)^{1/2}, which is at the limit of the good solubility region defined at $\Delta\delta \leq 5$ (MJ/m³)^{1/2}. ⁶⁶ The major difference between the linkages is caused by a difference in δ_d s with Priamine 1074/DGC having a higher value of 20.7 (MJ/m³)^{1/2} (versus 15.6 (MJ/m³)^{1/2} for PDMS-1k-(NH₂)₂/DGC). The dispersion forces are attractive forces, and hence, could have led to the segmentalization of Priamine 1074 and PDMS-1k-(NH₂)₂, during the polyaddition, in the presence of an abundant quantity of DGC. Since $\Delta\delta = 5.2$ (MJ/m³)^{1/2} $\cong 5$ (MJ/m³)^{1/2}, our previous conclusion on the miscibility of the soft segments of the TPHUs is confirmed.

On the other hand, the PDMS-XX25 TPHUs showed only one T_g with the lowest one exhibited by PDMS-4025 (-19 °C), which is not surprising as it contains the highest amount of PDMS-1k-(NH₂)₂. This suggests that, at a stoichiometric amount of DGC, the terpolymerization leads to segmented "statistical copolymers" made by Priamine 1074 and PDMS-1k-(NH₂)₂ connected with DGC units. The M_n and Đ increased with PDMS content, as shown in **Table 1**, and this is expected because PDMS-1k-(NH₂)₂ has a higher molecular weight than Priamine 1074, and its addition to the PHU chains lead to higher molecular weights and broadening of the distribution. As well, there is an increase in thermal stability of these TPHUs with the PDMS content (by 20 °C in T_{d,10%}), and their thermal stability is higher than their PDMS-XX40 analogs

(by as high as 40 °C in $T_{d,10\%}$). In fact, PDMS-XX25 have randomly arranged soft segments in their structure, so the PDMS units have more possibility to interact with the Priamine 1074 segments providing better thermal stability for these TPHUs with respect to their block copolymer (PDMS-XX40) analogs, in which the different blocks are far from each other, and thermally degrade one after the other (please refer to the TGA traces provided in Figure S5). The latter showed no improvement in thermal stability with increasing PDMS content either. The miscibility of the PDMS-1k-(NH₂)₂ and Priamine 1074 blocks strongly influences the interaction between the soft segments in the terpolymer structures. SAXS of these TPHUs were measured, and interdomain spacing (d) of 3.1-3.2 nm were calculated suggesting again that the hard segments are primarily causing the phase separation. Note that d of these samples slightly increased with the PDMS content like those of the PDMS-XX40 TPHUs. **Figure 1**-A and B summarizes the main results on the PDMS-based TPHUs discussed until this point.

TPHU	$M_n (g/mol)^a$	$\mathcal{D}=M_{w}/M_{n}^{a}$	$T_{g,l}$ (°C)	$T_{g,2}$ (°C)	T _{d,10%} (°C)	d ^b (nm)
PDMS-0040	5,800	2.6	-	-12	242	3.2
PDMS-2040	5,700	2.5	-32	-14	243	3.3
PDMS-4040	5,100	3.1	-30	-14	239	3.4
PDMS-0025	3,200	2.3	-16	-	256	3.1
PDMS-2025	4,700	3.2	-14	-	271	3.2
PDMS-4025	6,100	3.3	-19	-	279	3.2

Table 1. Structural and thermal properties of the PDMS containing TPHUs

a. Number average molecular weight and dispersities were estimated from SEC with THF eluent at 40 °C relative to poly(methyl methacrylate) standards.

b. The interdomain spacing (d) was calculated from Eq. (1).



Figure 1. Summary of structural phenomena observed in this study: A and B-segmented block and statistical copolymers, respectively formed during the terpolymerization of Priamine 1074 and PDMS-1k-(NH₂)₂ with excess and equimolar amounts of DGC, respectively, and Csegmented lamellae-like microstructure of DAD-4040 TPHU.

WAXS was conducted on the TPHUs of this section, and similar spectra were obtained for both sets of samples with differing amounts of PDMS. The WAXS spectra of the PDMS-XX25 and the PDMS-XX40 series are given as **Figure 2** and Figure S6, respectively, and they all present a peak at 20 around 14.5°, which is that of the Priamine 1074 phase. With increasing PDMS content, a distinct shoulder peak appears at 20 of 9° and increases in intensity with respect to the original peak. Previously, a distinct and sharp peak of PDMS in DGC and sugarbased dicarbonates PHUs appeared at 20 of 12.5° with a broad segmented PHU peak at 21.5°.^{25, ⁶⁹ As well, a 1,000 g/mol α,ω -PDMS diol had a sharp PDMS phase peak at 12.5°, ⁷⁰ which is interestingly higher than the 9° measured herein for a similar phase. Hence, the miscibility and interactions between the coexisting phases might have caused the decrease in the scattering angle of the PDMS phase, which aligns with the previous discussion.}



Figure 2. WAXS spectra of PDMS-0025, PDMS-2025, and PDMS-4025. The distinct shoulder peak at 2θ of 9° proving the presence of a PDMS phase in the microstructure of the TPHUs. The intensity is given in logarithmic scale.

The rheology of these TPHUs was also studied, and all of the PDMS-based TPHUs (except for PDMS-0040) showed a viscous-like behavior (G[°]) overcoming their elastic aspects (G[′]) at room temperature. A summary of the amplitude sweeps conducted on these samples is given in **Figure 3** (storage modulus, G[′]) and Figure S7 (loss modulus, G[°]). In **Figure 3**, G[′] increased with DGC and Priamine 1074, and decreased with higher PDMS content, proving our initial hypothesis on blending PDMS-1k-(NH₂)₂ with Priamine 1074. However, the decrease in G[′] was more significant in the PDMS-XX40 TPHUs, which might be due to the interaction of the Priamine 1074 and the PDMS soft segments randomly organized along the polymer chain of the PDMS-XX25 TPHUs. Hence, the effect of increasing the PDMS content on G[′] of the latter was reduced. The same reasoning was previously applied to discuss the increase in thermal stability of the PDMS-XX25 TPHUs, which is not observed in the segmented block copolymer-like PDMS-XX40 ones. Nevertheless, to extract fundamental information about the segmented TPHUS under study, frequency sweeps at various temperatures are conducted from which time-temperature superposition curves are obtained.



Figure 3. Storage modulus of the PDMS-based TPHUs collected from amplitude sweeps conducted at 22 °C and a frequency of 10 Hz.

The modulus reduced frequency curves are given as **Figure 4** to **Figure 6** and Figure S8 to Figure S10. The insets show the shift factors (a_T) used to construct the time-temperature superpositions from the frequency sweeps. The solid lines are approximate fits of the Generalized Maxwell model obtained using the least squares method and a procedure discussed elsewhere (Eqs. (3A.10) and (3A.11) of reference 71). ⁷¹ This model fits well the data; however, the data does not satisfy the terminal behaviour predicted by the model; slopes of 2 and 1 at low angular frequencies for G' and G", respectively, on a log-log scale, are not observed. Indeed, the terminal slopes of the storage modulus (G') are between 0.9 and 1.7 with no specific trend with changes in composition of the TPHUs. The terminal slopes of the loss modulus curves vary between 0.7 and 1 for all the PDMS-based TPHUs with a decreasing slope from 1 to 0.7 with increasing PDMS content in the PDMS-XX40 series and similar values between 0.8 and 0.9 for the PDMS-XX25 series. Previously, other models, e.g. the Rouse model, were used to fit frequency sweep data collected for segmented conventional PUs with deviations also observed. $^{40, 41}$ The shift factors obtained were fitted with the William-Landel-Ferry (WLF) equation: ⁷²

$$\log\left(a_{T_g}\right) = -\frac{c_1(T-T_g)}{c_2+T-T_g}$$
 Eq. (2)

which has been successfully used for homopolymers with universal constants $C_1 = 17.4$ and $C_2 = 51.6$ °C, which hold for temperatures between T_g and $T_g + 100$ °C. The chosen reference temperature was 70 °C (T_{ref}), from which the a_T of a given temperature was calculated as follows:

$$\log(a_T) = \log\left(a_{T_g}\right) - \log\left(a_{T_{ref}}\right)$$
 Eq. (3)

In the case of two T_{gs} , such as for the PDMS-XX40 TPHUs, the Fox equation was used to find an equivalent T_{g} seeing that the phases of the different soft segments are miscible. For PDMS- 0025 and PDMS-0040, the WLF equation fits well the used shift factors; however, the insets show its limitations in predicting accurate shift factors at low temperatures (up to 50 °C) with increasing PDMS content. Valenkar et al. observed a similar pattern when increasing the length of soft segment blocks of segmented PUs. ^{40, 41} Also, their time-temperature superposition broke down at low temperatures where the storage and loss moduli plots showed branches, but only the storage modulus plots of this study exhibited branches at high temperatures (above 90 °C) with an additional relaxation at a reduced angular frequency of 10 rad/s. Hence, the latter plot cannot be the result of a breakdown of the time-temperature superposition method, and a structural phenomenon has caused it, which will be shortly discussed.

Amorphous polymers exhibit two types of relaxation; a major α relaxation starting right after the T_g and minor relaxations (β , γ ...) occurring at temperatures lower than the T_g. ⁷² The PDMSbased PHUs have T_gs below 0 °C, and thus the relaxations observed in the time-temperature superposition of the present G' plots can be part of the α relaxations (typically known also as segmental or structural relaxations). In fact, the reduced angular frequency at 10 rad/s is spanned by temperatures ranging between 50 and 80 °C, and while DGC has a melting temperature at 65 °C, this new relaxation can be caused by the "flow" of hard segments, as it was previously indicated that DGC is the major cause of nanophase separation in the PDMS-based TPHUs. Beniah et al. observed similar trends after performing dynamic mechanical thermal analysis (DMTA) on their nanophase separated segmented PHUs. ⁴⁴⁻⁴⁹ Besides, the flow of the hard segments at 65 °C might have led to the branches at temperatures above 90 °C since the slopes of the curves gradually decreased when going from 80 °C to 120 °C, which is a sign of chain softening and reorganization. The shift factors were also fitted using the Arrhenius law equation to find the activation energy: ⁷²

$$\ln(a_T) = \frac{E_A}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)$$
Eq. (4)

where E_A is the activation energy for the viscoelastic relaxation, R is the gas constant (8.314 J/mol.K), and T_{ref} was previously defined as 70 °C. It is found that, contrary to the WLF equation, the Arrhenius law fits best the shift factors of the TPHUs containing PDMS ($R^2 = 0.99$). The calculated activation energies decreased with PDMS content (please check Figure S8 to Figure S10 as well), and this is expected as a higher PDMS content softens the TPHUs and decreases the T_g , and E_A is the required energy to overcome the glass transition and achieve chain motion.

After characterizing the PDMS-based TPHUs, the next section briefly presents the impact of adding DAD on a DGC/Priamine 1074 PHU.



Figure 4. Dynamic mechanical frequency sweep data for PDMS-0040 (G" curve is shifted by a factor of 5) at 0.5% shear strain. The solid line is a fit to the Generalized Maxwell model. The inset shows the shift factors used for time-temperature superposition. The solid and dashed lines in the inset are the WLF and Arrhenius law fit equations, respectively.



Figure 5. Dynamic mechanical frequency sweep data for PDMS-2040 (G" curve is shifted by a factor of 5) at 0.5% shear strain. The solid line is a fit to the Generalized Maxwell model. The inset shows the shift factors used for time-temperature superposition. The solid and dashed lines in the inset are the WLF and Arrhenius law fit equations, respectively.



Figure 6. Dynamic mechanical frequency sweep data for PDMS-4040 (G" curve is shifted by a factor of 5) at 0.5% shear strain. The solid line is a fit to the Generalized Maxwell model. The inset shows the shift factors used for time-temperature superposition. The solid and dashed lines in the inset are the WLF and Arrhenius law fit equations, respectively.

Characterization of DAD containing TPHUs

Previously, it was reported by Magliozzi et al. that the equimolar reaction of DGC with DAD, after 4 h at temperatures between 80 and 95 °C using magnetic stirring, resulted in a 41% conversion of DGC. ¹⁸ The DAD-TPHU reactions conducted herein with 40 wt.% DGC operate at nearly equimolar ratios as well, so it is anticipated that at the applied reaction conditions (80 °C and 24 h), the conversion of DGC will be above 90%, and that was confirmed by FTIR in which the DGC carbonyl stretch (at 1790 cm⁻¹) disappeared completely for DAD-3040 and DAD-4040 (Figure S11). The DAD-##55 series showed a substantial fraction of unreacted monomers, mainly DGC and DAD, at the adopted reaction conditions, so the samples were disregarded from this study. The conversion of DAD-0040 was discussed previously (that of PDMS-0040). Similar to the PDMS containing TPHUs, the secondary hydroxyl groups content decreased when running the terpolymerizations with DAD, as analyzed from ¹H-NMR (please refer to Figure S12 and Table S3 for more details). Note that the naming of the TPHUs adopted herein is similar to the one used previously for the PDMS-based TPHUs.

Table 2 summarizes the structural and thermal properties of the DAD-based TPHUs. It is clear that blending DAD with Priamine 1074 led to higher M_n with low D (about 2.5) with increasing DAD content. Because DAD is significantly shorter than Priamine 1074 and PDMS-1k-(NH₂)₂, DAD acts as a chain extender of the DGC/Priamine 1074 PHUs, as confirmed by the SEC results in **Table 2**. Besides, DAD is more rigid than Priamine 1074, so its incorporation in the TPHU structure leads to chains with lower mobility as reflected by the slightly higher T_g values (-5 °C) of the DAD TPHUs versus DAD-0040 (-12 °C). The thermal stability of DAD-0040 was also improved with the addition of DAD, and $T_{d,10\%}$ increased by 20 °C (refer to the TGA traces provided in Figure S13). However, neither the T_g nor the thermal stability were dependent on the

DAD concentrations. Interestingly, all the DAD TPHUs are semi-crystalline with a crystalline fraction (X_c) between 7.5 and 9%, which were calculated from the WAXS spectra of Figure S14 using the deconvolution method. However, only DAD-4040 exhibited a semi-crystalline behavior when tested on DSC with a melting temperature (T_m) at 67 °C and heat enthalpy (ΔH_m) of 19.3 J/g, and its crystallinity matched the one calculated from WAXS (Table 2). DSC might have failed to detect the crystallinity of the other samples because of the lower content of DAD and hence lower contrast between the amorphous (Priamine 1074/DGC) and crystalline (DAD/DGC) phases. Moreover, DAD-4040 exhibited a crystallization temperature (T_c) at 32 °C and a heat enthalpy (ΔH_c) of -20.5 J/g, from DSC, with an onset temperature at 19 °C, which implies that the chains of this TPHU, along with those of DAD-2040 and DAD-3040, are mobile at room temperature and rearrange into ordered microstructures. That was actually confirmed from the SAXS measurements of Figure 7, in which the spectra present higher order diffractions with no specific pattern for DAD-2040 and DAD-3040 and a lamellae-like pattern for DAD-4040 (ratio q/q* of 1, 2, 3 pattern). ⁷³ In fact, DAD-4040 is extremely brittle, such that its samples could not be cut out of the mold for mechanical testing as they shattered immediately (it was very glassy). This qualitative observation matches the microstructural pattern uncovered for DAD-4040, which has its chains parallelly aligned with respect to one another (Figure 1-C). Still, mechanical testing was carried out on the softer DAD-2040 and DAD-3040, and the results are presented in **Figure 8**. The segmentation of the DAD-based TPHUs is clearly observed from the shape of the stress-strain curves, which have two subsequent deformations: the first one for the amorphous phase followed by the deformation of the crystalline phase which yields before the sample breaks. DAD-3040, containing more DAD, broke at a lower elongation at break (EB%) of 16% \pm 7 with respect to DAD-2040 (37% \pm 4). The DAD content also affected the

Young's modulus of the second deformation while the Young's moduli of the amorphous phase (first deformation) were close for both samples (0.39 MPa \pm 0.16 MPa for DAD-2040 and 0.33 \pm 0.03 MPa for DAD-3040). Actually, the effective Young's moduli for the crystalline phase were higher for DAD-3040 (0.12 \pm 0.02 MPa) as it comprises 10 wt.% more of DAD with respect to DAD-2040 (0.08 \pm 0.04 MPa). Moreover, the amplitude sweeps on these samples showed a significant increase in storage modulus (G') (200 to 800 times) when going from DAD-0040 to DAD-4040 as shown in **Figure 9** and Figure S15.

Noting the semi-crystallinity of the DAD-based TPHUs and their structural complexity, only the PDMS-based TPHUs were selected to be blended with PLA, and the results are discussed in the next section.

TPHU	$M_n (g/mol)^a$	$\mathcal{D}=M_w/M_n^a$	$T_g(\mathcal{C})$	$X_{c,DSC}^{b}$ (%)	$X_{c,WAXS}^{c}$ (%)	T _{d,10%} (°C)
DAD-0040	5,800	2.6	-12	-	-	242
DAD-2040	5,100	3.1	-5	-	7.5	260
DAD-3040	6,300	2.7	-7	-	8.8	266
DAD-4040	8,200	2.4	-4	8.8	8.4	262

Table 2. Structural and thermal properties of the DAD containing TPHUs

a. Number average molecular weight and dispersities were estimated from SEC with THF eluent at 40 °C relative to poly(methyl methacrylate) standards.

b. The crystallinity X_c was calculated from DSC by dividing $\Delta H_m = 19.3 \text{ J/g}$ with $\Delta H_{m,100\%} = 219 \text{ J/g}$ of DAD as crystallinity was caused by the addition of DAD. $\Delta H_{m,100\%}$ of DAD was estimated by interpolation from the $\Delta H_{m,100\%}$ of 1,12-diaminododecane and 1,6-hexamethylene diamine.⁷⁴

c. The crystallinity X_c was calculated from WAXS by using the deconvolution method to estimate the area of the amorphous and crystalline portions. X_c was found by taking the ratio of the crystalline area over the total area.



Figure 7. SAXS spectra of DAD-based TPHUs showing ordering in their microstructure. The intensity is given in logarithmic scale.



Figure 8. Tensile test results of the semi-crystalline DAD-2040 and DAD-3040 showing the stretching of the amorphous phase first followed by the crystalline phase before yielding and breaking.



Figure 9. Storage modulus of the DAD-based TPHUs collected from amplitude sweeps conducted at 22 °C and a frequency of 10 Hz.

Blends of PLA with bio-based TPHUs

Blending PLA with the following TPHUs; PDMS-0040, PDMS-2040, PDMS-2025, and PDMS-4025, (80/20 wt.%/wt.%) resulted in an increase in PLA flowability and viscous properties, as was observed from the amplitude sweeps conducted on the samples at room temperature (~22 °C) and the temperature of extrusion (150 °C). Figure S16 shows that the TPHUs did not affect the storage modulus of PLA while increasing its loss modulus and hence its viscous properties. This is more pronounced when running the amplitude sweeps at 150 °C, at which the flow point of the blends was reached at lower shear strains when compared to PLA (Figure S17). Frequency sweeps were also conducted on the blends and their components at room temperature (shear strain of 0.01% and 0.1-100 Hz) and 150 °C (shear strain of 5% and 0.1-100 rad/s) to quantify the complex viscosities. The linear mixing rule was used to calculate the complex viscosities of the blends from the components: ⁶³

$$\eta_{1,2}^* = \phi_1 \eta_1^* + \phi_2 \eta_2^*$$
 Eq. (5)

where ϕ_1 and ϕ_2 are the weight ratios of species 1 and 2, respectively, and η_1^* and η_2^* are the viscosities of the two species. Then, the calculated complex viscosities of the blends were compared to the experimental ones, and error differences between 6 and 44% were found, which suggests that the blends are partially miscible, and that is expected based on Lin et al.'s study on blending PLA with hyperbranched poly(ester amide). ⁶³ This partial miscibility was observed from DSC (**Table 3**), which showed two T_gs for the blends; one for the TPHUs between -9 and -5 °C and a second for PLA between 53 and 58 °C. The component T_gs of the TPHUs were shifted more significantly with the T_gs of PDMS-2025 and PDMS-4025 shifting more, and to higher values, because they contain fewer hard segments and hence flow easier in the PLA matrix during the extrusion process. Nevertheless, the T_g of PLA did shift to lower values, and

that in blends containing PDMS-0040 and PDMS-4040 only, as observed from the DSC and DMTA (please see Figure S18 to Figure S20) results of **Table 3**. This means that PDMS-0040 and PDMS-4040 are potential plasticizers/softeners of PLA, and they hold a structural feature giving them this advantage over their lower hard segment content counterparts.

Method		DSC				$DMTA^{a}$		
Blend	$T_{g,1}^{b}(^{\circ}C)$	$T_{g,2}$ (°C)	T _m (°C)	$\Delta H_m \left(J/g \right)$	X _c ^c (%)	T _{g,2} ^(G'') (°C)	$T_{g,2}^{(tan\delta)}$ (°C)	
PLA only ^d	-	58	152	1.3	1.8	61	65	
PLA/PDMS-0040	-9 ± 1.0	53 ± 1.6	$\begin{array}{c} 150 \pm \\ 1.0 \end{array}$	3.7 ± 1.4	4.9 ± 1.9	54	58	
PLA/PDMS-2040	-8 ± 0.6	54 ± 1.2	-	-	-	51	57	
PLA/PDMS-2025	-6 ± 0.5	57 ± 0.4	-	-	-	61	64	
PLA/PDMS-4025	-5 ± 1.0	58 ± 1.0	-	-	-	60	63	

Table 3. Thermal transitions of the blends of this study (80/20 wt.%/wt.%)

a. DMTA was only capable of detecting the second T_g of PLA due to equipment limitations as cooling samples to temperatures below room temperature (22 °C) were not possible.

b. T_{g,1} for PLA/PDMS2040 had low intensity with respect to T_{g,2} compared to other blends.

c. The crystallinity X_c was calculated from DSC by dividing ΔH_m with $\Delta H_{m,100\%} = 93.6$ J/g of PLA multiplied by the weight fraction of PLA (0.8 in this case for all the blends). ⁵⁹

d. The PLA samples was extruded at similar conditions as the blends.

To unveil this structural feature, the FTIR spectra of the TPHUs were examined, and it was found that, in the region of 1650 to 1850 cm⁻¹, there exists a distinct carbonyl stretch at 1790 cm⁻¹ which suggests the presence of cyclic carbonate end-groups in the chains of PDMS-0040 and PDMS-2040 (Figure S21). This is not surprising as, at 40 wt.% DGC content, the reactions

leading to these TPHUs were conducted with excess DGC. The ratios of the C=O stretches of the cyclic carbonates to those of the urethane linkages, $R_{C=O}^{TPHU}$, were calculated using the deconvolution method of the peaks, and are summarized in **Table 4**. It is possible that the abundant cyclic carbonate end-groups in PDMS-0040 and PDMS-2040 interact via hydrogen bonding with the hydroxyl end-groups of PLA. This affects the entanglements and the mobility of the PLA chains, which decreases their T_g. A similar explanation was proposed by Kuan et al., who studied multi-wall carbon nanotube/PLA composites. ⁷⁵ Therefore, the FTIR spectra of the blends (Figure S22 and Figure S23) were also examined to estimate the fraction of carbonyl groups participating in hydrogen bonding, $f_{c=0}^{b}$, in each of the blends. This parameter was found from the equation below:

$$f_{c=0}^{b} = \frac{A_{b}/1.5}{\frac{A_{b}}{1.5} + A_{f}}$$
Eq. (6)

where A_f and A_b are peak areas corresponding to the free and hydrogen bonded carbonyl groups, respectively, calculated using the relative areas of the C=O stretches of PLA and the TPHUs with other distinct peaks in their structure. The deconvolution method would have been better for the purpose of these calculations, but the C=O of the urethane linkages overlapped with the rest of the carbonyl stretches, which made the deconvolution of the peaks difficult to be applied. The conversion coefficient 1.5 is the ratio of these two bands in an ester group. ⁶³ The values of $f_{c=0}^{b}$ are summarized in **Table 4**, and they were found to be significantly lower than those calculated in a previous study by Lin et al. (37%) on poly(ester amide)/PLA systems because these authors had more sites in their hyperbranched poly(ester amide) available for hydrogen bonding. ⁶³ Indeed, the hydrogen bonding effects of the blends studied here are diluted by the structure of the soft segments used to synthesize the TPHUs. $f_{c=0}^{b}$ was almost the same for all the blends except of PLA/PDMS-2025, in which the fraction of hydrogen bonded C=O is approximately half the values of the other blends. PLA/PDMS-4025 had a similar $f_{c=0}^{b}$ to the PLA/PDMS-0040 and PLA/PDMS-2040, containing TPHUs with abundant carbonate end-groups, because there exist other sites in a TPHU that can undergo hydrogen bonding with PLA, such as the NH groups of the urethane linkage and the hydroxyl groups that can interact with the carbonyl groups of PLA. The hydrogen bonding interactions were verified from FTIR by the broadening of the C=O stretch of PLA (Figure S22) as well as the formation of a broad OH band in the 3000 to 3500 cm⁻¹ region (Figure S23).

One of the main purposes of blending PLA with other additives is to increase its toughness or associated property such as impact strength; hence, the mechanical properties of the blends were measured, and they are presented in Table 4 and Figure 10. Note that the mechanical properties obtained for PLA were akin to a previous study that used a similar method for preparing the films of this study. ⁶⁴ The Young's modulus (E) and the tensile strength (σ_{max}) were not affected by the addition of the TPHUs into the PLA matrix, which confirms the amplitude sweep results discussed in the beginning of this section. Only PLA/PDMS-2040 showed a drop in E with no tensile strength, maybe due to the type of hydrogen bonding interactions occurring in this blend (discussed in the sub-section above). However, only two blends showed an increase in the toughness of PLA; PLA/PDMS-2040 and PLA/PDMS-4025, whereas the films of the other two blends broke at low elongations at break (EB%) of 40 and 60%. This suggests that some of these blends might be immiscible, so the relative energy differences (RED) of the blends were calculated (Table 4) using the solubility parameters estimated from the group contribution method conducted earlier (please see Tables S4 and S5). An RED value less than 1 is desired for the blends to be considered miscible, ⁷⁶ so since the RED values of the blends are around 1, it means that they are partially miscible as it was previously deduced. PLA/PDMS-0040 has the

highest value of 1.2, which explains its low EB%. PLA/PDMS-2025 has an RED at the limit of phase miscibility, and since it has the lowest $f_{c=0}^{b}$, it does not have the necessary interfacial strength, leading to the lowest EB%. The remaining two blends have the highest $f_{c=0}^{b}$, and their REDs are at the limit of phase miscibility, so they ended up slightly increasing the toughness of PLA by increasing the EB% to 300%. We expected the blending to be aided by the functional groups on the PLA and the TPHU, which could have provided the interactions needed to compatibilize the blends.

Table 4. Structural, mechanical, and miscibility properties of the blends of this study (80/20wt.%/wt.%)

Blend	$R_{C=O}^{TPHU}$	$f^{b}_{c=0}$ (%)	E (MPa)	σ_{max} (MPa)	EB (%)	RED^{a}	
PLA only	-	-	2.22 ± 0.32	9.50 ± 1.23	262 ± 39	-	
PLA/PDMS-0040	0.42	8.2	2.75 ± 0.45	10.1 ± 1.00	61 ± 22	1.2	
PLA/PDMS-2040	0.50	9.7	1.16 ± 0.09	-	305 ± 55	1.0	
PLA/PDMS-2025	0.28	4.2	2.64 ± 0.21	11.9 ± 1.62	39 ± 9.3	1.0	
PLA/PDMS-4025	0.06	9.6	3.09 ± 0.38	11.9 ± 1.85	297 ± 49	0.88	

a. Please refer to Section IV of the supporting information for more information on how to obtain the RED of the blends.



Figure 10. Stress-strain curves of the PLA/TPHU blends of this study (80/20 wt.%/wt.%).

Finally, the blend morphologies were examined through SEM, and Figure 11 presents the SEM of their cryogenically fractured surfaces, untreated and treated with THF (to selectively remove one component from the other). It is seen from the SEM of the untreated surfaces that the TPHUs with higher DGC content are more compatible with PLA. A similar observation was made elsewhere where the authors blended PLA with TPUs of different solid contents, and the higher solid content TPUs showed a finer phase morphology in PLA. The TPHUs droplets that got pulled out from PLA/PDMS-2025 and PLA/PDMS-4025 were slightly bigger and outnumber the ones resulting from cryo-fracturing of PLA/PDMS-0040 and PLA/PDMS-2040. Actually, all of the blends were already found to be partially miscible, and PDMS-0040 and PDMS-2040

were previously stated as being more rigid and exhibiting hydrogen bonding with PLA via endchain interactions. However, these droplets can be misguiding, as they can also result from artifacts of the fracturing process; hence, we treated the surfaces with THF to remove the TPHU phase and get more accurate information about the morphology of the blends. Interestingly, the SEM of PLA/PDMS-0040 and PLA/PDMS-2040 had better defined sphere-shaped dispersion of the TPHUs in the PLA matrix, whereas the remaining blends had TPHUs of lower hard segments forming a co-continuous-like phase with PLA. The hard segment content of the TPHUs plays a major role in forming these phases, as PDMS-0040 and PDMS-2040 are more rigid and can better disperse in the PLA matrix at the extrusion temperature of 150 °C. On the other hand, PDMS-2025 and PDMS-4025 are softer, as previously discussed from **Figure 3**, so they tend to flow more at 150 °C, and end up forming bigger droplets that coalesce, which results in cocontinuous-like phases of PLA and these TPHUs.



Figure 11. SEM of cryogenically fractured surfaces of PLA/TPHUs blends (80/20 wt.%/wt.%) untreated and treated with THF to remove the TPHUs phase solely (5000 magnification).

CONCLUSIONS

Terpolymerizations based on DGC and Priamine 1074 were conducted by blending Priamine 1074 with PDMS-1k-(NH₂)₂ or DAD at different ratios and with different hard segment (DGC) contents. The PDMS-based TPHUs with higher DGC content (40 wt.%) presented a block copolymer-like segmented structure and two T_gs. The remaining TPHUs of lower DGC content (25 wt.%) showed an increase in thermal stability resulting from the alternation of soft segments in the TPHU structure. Additionally, Priamine 1074 and PDMS-1k-(NH₂)₂ soft segments were fairly miscible in the TPHU microstructure, based on the Hoftyzer-Van Krevelen's group contribution method used to estimate the Hansen solubility parameters, with nanophase separation caused mainly by the presence of DGC. The rheology of these TPHUs revealed that the PDMS-based TPHUs of higher hard segment content had higher storage modulus than their lower hard segment content analogs. As well, the presence of DGC was obvious from dynamic frequency sweeps and time-temperature superpositions, in which an additional relaxation, caused by the melting of the DGC linkages in the TPHUs at ~65 °C, was present.

The addition of DAD into Priamine 1074, during the terpolymerization, led to a new class of fully bio-based semi-crystalline TPHUs with crystallinity fractions of about 8%. The presence of DAD introducing crystallinity was observed in the evidence of microstructural ordering of the TPHUs, as revealed by SAXS. Being a shorter diamine, DAD acted as a chain extender during the synthesis of DAD-4040, and added the rigidity needed to the DGC/Priamine 1074 matrix with the storage modulus significantly increasing with the DAD content.

At last, the blends of PLA with some of the PDMS-based TPHUs were prepared. The blends were found to be partially miscible based on different characterization techniques: rheology, DSC, Hoftyzer-Van Krevelen's group contribution method to estimate relative energy differences (RED) between PLA and the TPHUs, and SEM. PDMS-0040 and PDMS-2040 acted as plasticizers of PLA, and this is due to the type of hydrogen bonding interactions exhibited by the TPHUs/PLA systems; through the end-chain carbonate of the TPHU and hydroxyl groups of the PLA, respectively. The tensile properties of the blends revealed that PDMS-2040 and PDMS-4025 increased the toughness of PLA and that is based on different factors; highest amount of hydrogen bonding ($f_{c=0}^{b}$) and lowest RED. The SEM presented a co-continuous morphology of the blends of PLA with the lower hard segment TPHUs, compared to a dispersed phase of the higher hard segment analogs in the PLA matrix, and that was related to the softer character of the former and their tendency of mixing better with PLA during the extrusion process.

To our knowledge, this study is the first to prepare PHUs from terpolymerizations and to investigate their rheology and blending with PLA. Our study can be used as a stepping point to synthesize new families of fully/partially bio-based TPHUs and blend them with bio-based polymers like PLA.

ASSOCIATED CONTENT

Supporting Information.

The supporting information is available free of charge at...

DGC ¹H-NMR spectrum, FTIR and ¹H-NMR of PDMS containing TPHUs, Group contribution method estimating solubility parameters of PDMS-based TPHUs, TGA traces and WAXS of PDMS-based TPHUs, rheology of PDMS containing TPHUs, FTIR and ¹H-NMR of DAD containing TPHUs, TGA traces and WAXS spectra of DAD containing TPHUs, rheology of PLA/TPHU blends, FTIR of TPHUs and PLA/TPHU blends, miscibility analysis of PLA/TPHU blends (RED calculations) (PDF)

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Notes

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