Incorporation of Poly(Dimethylsiloxane) into Poly(Tetramethylene Oxide) Based Polyurethanes: The Effect of Synthesis Conditions on Polymer Properties

Maryline Rochery[a]; Isabelle Vroman[a]; Thanh My Lam[a]

[a] Laboratoire de GEnie et Matériaux TEXtiles (GEMTEX), UPRES EA2161, Ecole Nationale Supérieure des Arts et Industries Textiles (ENSAIT), Roubaix cedex, France

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Maryline Rochery, Isabelle Vroman,* and Thanh My Lam

Laboratoire de GEnie et Matériaux TEXtiles (GEMTEX),
UPRES EA2161, Ecole Nationale Supérieure des Arts et Industries
Textiles (ENSAIT), Roubaix cedex, France

ABSTRACT

Two procedures for incorporating low levels of poly(dimethylsiloxane) (PDMS) in polyurethane (PU) have been studied. The bulk synthesis of poly(siloxane-urethane) was performed in two steps: the first involves the formation of a prepolymer between isophorone diisocyanate (IPDI) and poly(tetramethylene oxide) (PTMO). In the second step 1,4-butanediol (BD) was added as the chain extender. A kinetic study followed by infrared spectroscopy showed the higher reactivity of PDMS compared to PTMO. Thus, two procedures for incorporating PDMS are described, depending on whether the poly(dimethylsiloxane) was introduced in the first or in the second step. Films were made from these formulations, and we studied their morphology. The products obtained from each procedure were characterized by size-exclusion chromatography (SEC), differential scanning calorimetry (DSC), dynamic thermomechanical analysis (DMTA) and uniaxial tensile testing, and showed significant differences. These poly(siloxane-urethane) polymers are intended to be used as hydrophobic coated formulations on polyester fabrics in a further study.

*Correspondence: Isabelle Vroman, Laboratoire de GEnie et Matériaux TEXtiles (GEMTEX), UPRES EA2161, Ecole Nationale Supérieure des Arts et Industries Textiles (ENSAIT), 9 rue de l'Ermitage, BP 30329, 59056 Roubaix cedex 01, France; E-mail: isabelle.vroman@ensait.fr.

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Key Words: Poly(siloxane-urethane); Poly(dimethylsiloxane); Morphology; Thermal properties.

INTRODUCTION

Polyurethanes (PUs) are synthetic materials, well known in the field of research and largely used in industry because of their numerous properties. In particular, they are used for textile coatings because of their mechanical properties. Poly(dimethylsiloxane)s (PDMS) are largely used as additives to improve the mass and/or surface properties of polymeric materials. PDMS have indeed interesting surface properties such as a high water repellency and a low surface energy.[1] Siloxanes can be incorporated into polyurethanes in order to obtain new hydrophobic formulations. Several studies have been carried out on the formulation of PDMS-PUs.[2−7] In some of these references,[2−4] the isocyanate used was 4,4′-diphenylmethane diisocyanate (MDI), and they made use of only one polyol, PDMS, the polycondensation being performed in solution. When the thermoplastic polyurethane elastomers were synthesized with a mixture of macrodiols,[5] the PDMS ratio was higher than 15 wt%. The synthesis of PDMS-PU via solution polymerization is difficult due to the large solubility differences between the dimethylsiloxane and urethane components in the reaction medium. Our approach is to synthesize the PUs in bulk, without solvent. This is very interesting for the industry because bulk synthesis has a low environmental impact and generally a lower cost. Two studies have been reported, dealing with a one-step bulk polymerization[8] or a two-step bulk polymerization.[9] MDI was used as isocyanate and the PDMS ratio was at least 25 wt%. In this work, we used isophorone diisocyanate (IPDI) as isocyanate, chosen because of its easy handling (liquid at room temperature). The soft segments were based on a mixture of hydroxy-terminated poly(dimethylsiloxane) and poly(tetramethylene oxide) (PTMO). A low level of PDMS (2 wt%) was chosen for a further application in hydrophobic coating.[10] A kinetic study of the reaction of polycondensation was first performed in order to define the appropriate moment for the incorporation of the PDMS. From this study we chose a model formulation, and studied two procedures for incorporating poly(dimethylsiloxanes). The products obtained were then characterized by a range of physical techniques, allowing an evaluation of the efficiency of the two methodologies.

EXPERIMENTAL

Materials

IPDI from Aldrich was used without further purification. PTMO also provided by Aldrich, with an average molecular mass $\overline{M_n}$ of 1000 or 2000 g mol^{-1}, was dried under vacuum at 70°C for 24 h before use. Hydroxy-terminated PDMS (H-Si2111 and H-Si2311, of average molecular mass 900 and 2500 g mol^{-1}, respectively) were supplied by Goldschmidt Co., France. Their formula and molecular mass are given in Table 1. 1,4-butanediol (BD) and dibutyltin dilaurate (SnDBL) were used as chain extender and catalyst, respectively. Both of them were obtained from Aldrich.

Table 1. Chemical structures of hydroxy-terminated poly(dimethylsiloxanes) used in this study.

Chemical structure	Commercial name	Abbreviation in this paper	Molecular mass
$HO-(CH_2)_m$ $\begin{bmatrix} \overset{CH_3}{\underset{CH_3}{\mid}} \\ Si-O \\ \mid \end{bmatrix} \begin{matrix} CH_3 \\ \mid \\ Si-(CH_2)_m-OH \\ \mid \\ CH_3 \end{matrix}_n$	H-Si 2111	PDMS 900	$\overline{M_n} = 900 \, g \cdot mol^{-1}$
	H-Si 2311	PDMS 2500	$\overline{M_n} = 2500 \, g \cdot mol^{-1}$

Polymer Syntheses

The synthesis was carried out in a three-necked round-bottom flask equipped with a high torque stirrer, a nitrogen inlet and an outlet. The temperature of the reaction was 100°C and was controlled by immersion in an oil bath. The mole ratio of PTMO, IPDI and (BD + PDMS) was 1/2/1. The PDMS was introduced either with the PTMO (PU noted PU-PDMS❶) in the first step or with BD in the second step (PU noted PU-PDMS❷). PTMO was introduced first into the flask, and was then degassed. IPDI was then added. A prepolymer was obtained after 24 h. BD was added and after stirring, the mixture was cast in a preheated mold 2 mm thick. The reaction was completed by curing the plate for 72 h at 80°C. No catalyst was used in the bulk synthesis. The Sn catalyst was used only for the kinetic study of the reaction between IPDI and the polyols (see below).

Characterization

Kinetic Follow-Up by Infrared Spectral Analysis

A mixture of diisocyanate and macrodiol (PDMS or PTMO) was first prepared with or without catalyst in stoichiometric proportions. The Sn catalyst was introduced at a 0.2 wt% concentration. The mixture was stirred vigorously for 1 min, then a drop was put between two KBr plates. The disks were then placed in a heating cell (Harrick) and the reaction mixture was followed on a Perkin Elmer Model 1600 Fourier transform infrared (FT-IR) spectrometer. Several spectra were taken during the reaction. Scanning resolution was $4 \, cm^{-1}$ and 16 scans were averaged to obtain each spectrum.

Size-Exclusion Chromatography (SEC)

Molecular weight analysis was carried out on a Waters model 510 chromatograph equipped with a U6K injector, a R410 differential refractometric detector and 4 Ultrastyragel columns (100, 500, 10^3, 10^4 Å) operating at room temperature. Tetrahydrofuran (THF) was used as the mobile phase and the flow rate was maintained at $1 \, ml \, min^{-1}$. Samples were prepared at a 0.5 wt% concentration. The system was

calibrated against 5 narrow distribution polystyrene standards. Results are therefore expressed as polystyrene-equivalent molecular weights.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed on a Polymer Laboratories DSC heat flux calorimeter that has been calibrated for heat flow (standard saphire) and temperature (benzophenone, standard indium, tin, lead and zinc). The samples of about 10–15 mg each were placed in aluminium pans. They were first dried at 105°C for 5 min to remove maximum moisture and then quenched to -140°C in the DSC cell. They were then heated at a rate of 10°C·min^{-1} up to 200°C. Glass transition temperatures were determined from the point of intersection between the tangent to the curve at the starting point and the tangent to the point of infexion in the glass transition region.

Thermomechanical Analyses

Measurements were acquired on a MKIII DMTA from Polymer Laboratories, using the single canti-lever flexure mode at a frequency of 1 Hz. The strain amplitude was fixed to a selected value of 32 µm, and the sinusoidal stress amplitude and the phase shift were measured, in order to obtain the elastic modulus G' and the loss tangent δ. Samples were cooled quickly to -100°C by liquid nitrogen and scans were run from -100°C to 150°C with a heating rate of 3°C min^{-1}. The typical length of the test specimens were about 8–10 mm with rectangular lateral dimensions of about 10×2 mm. The DMTA apparatus was calibrated before measurements: the dynamic mechanical conversion constant and the transducer factor were checked once a week, whereas the baseline correction values were determined daily.

Uniaxial Tension

The uniaxial stress–strain testing was performed at room temperature on a Zwick model 1456 tensile testing machine equipped with "8222" grips and a 10 kN load cell. The cast PU sheets of about 2 mm thick were cut into small dumbbells of 50 mm in length to allow high elongation. The narrow section was 4 mm in width. Run conditions were established from the ISO R 527 standard procedure: the tensile tests were performed at the crosshead speed of 400 mm min^{-1} for specimen with high elongation (more than 600%) or 50 mm min^{-1} for the other ones so that breakdown occurred in 30 ± 1 sec. A 19 mm gauge length and original cross-sectional area were utilized to calculate their tensile properties. The results reported for the initial modulus (E_0), the tensile stress at break (σ_b), and the ultimate elongation (ε_b) are the mean values for 5 replicates. The experimental error is estimated within $\pm 15\%$.

RESULTS AND DISCUSSION

Kinetic Study

A kinetic study by FT-IR of a mixture of IPDI and PDMS (900 or 2500) and of a mixture of IPDI and PTMO (1000 or 2000) was carried out, in order to compare the reactivity of the two types of macrodiols. It consists in following the disappearance of the characteristic peak of the isocyanate group located at a wave number $\bar{v}$ close to $2257 \, cm^{-1}$. The extent of the reaction noted r[NCO] is given by the relation below:

$$r[NCO] = \frac{[NCO]_0 - [NCO]}{[NCO]_0} = 1 - \frac{A(NCO)[t]}{A(CH_2)[t]} : \frac{A(NCO)[t_0]}{A(CH_2)[t_0]}$$

where $[NCO]_0$ is the initial concentration of NCO, $A(NCO)[t_0]$, $A(NCO)[t]$ are the integrated absorbance of NCO respectively at the initial time (t_0) and at any time "t" of the reaction, $A(CH_2)[t_0]$, $A(CH_2)[t]$ are the integrated absorbance of CH_2 respectively at the initial time and at any time "t" of the reaction.

The band relating to the CH_2 groups (between 2600 and $3030 \, cm^{-1}$) is taken as reference, and is considered not to evolve with time. The initial time t_0 corresponds to the spectrum of the mixture after a few minutes of stirring at ambient temperature and is not exactly the same for several replicates: kinetic data-errors are estimated to 10%. The follow-up of kinetics by FT-IR are reported on Fig. 1. The curves show that the $\overline{M}_n$ value
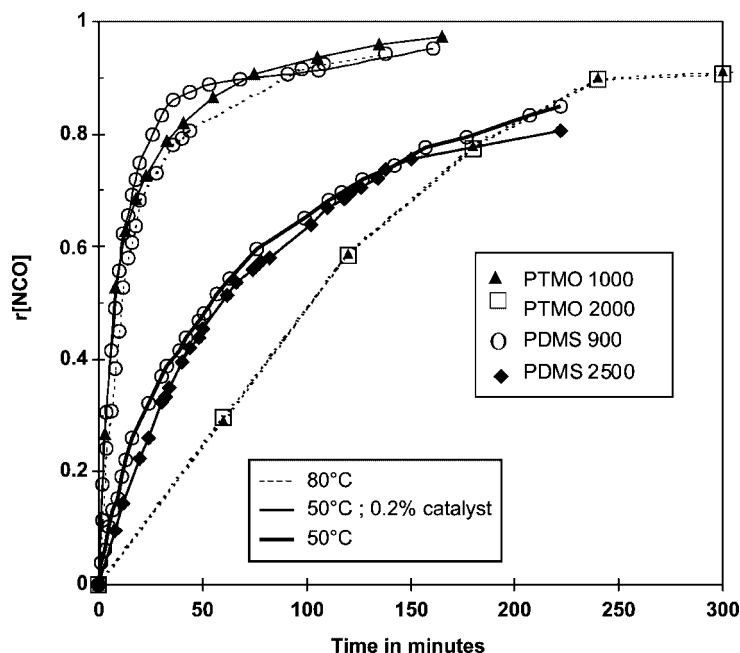
Figure 1. Comparison of the curves giving the advancing rate of the reaction as a function of time, r[NCO] = f(t) for IPDI/PTMO and IPDI/PDMS mixtures at 50°C and 80°C with or without catalyst.

of the macrodiols does not have a significant influence on the extent of the reaction. A superposition of the curves is indeed observed for the mixtures of IPDI/PTMO 1000 and IPDI/PTMO 2000 at 80°C, as well as for the mixtures of IPDI/PDMS 900 and IPDI/PDMS 2500 at 50°C. The PDMS is more reactive than the PTMO: the difference is very obvious at 80°C, where in the case of PDMS, 80% conversion of the isocyanate functions is reached after 50 min with PDMS vs. 200 minutes with PTMO. On the other hand, at 50°C with 0.2% of catalyst, both macrodiols have equivalent reactivities with respect to IPDI; it is thus possible to consider formulations where they would be introduced at the same time to allow a statistical distribution of the two reagents within the macromolecular chains. It is interesting to note that in the case of PDMS 900, the change in the temperature from 50°C to 80°C produces the same effect as the addition of 0.2 wt% catalyst at 50°C. The curves r[NCO] = f(t) are indeed relatively close.

Choice of the Formulations and Conditions of Synthesis

The synthesis was carried out by the conventional two-step prepolymer method. A polyetherdiol was chosen as macrodiol, because it has a greater resistance to hydrolysis than polyesterdiols.[11,12] Moreover, the use of a polar polyol (polyetherdiol or polyesterdiol) with short chains favors the mixture of phases[13,14] and the kinetic study showed that the extent of the reaction is independent on the macromolecular mass of the macrodiol, so PTMO 1000 was used. Diols as BD are the classical chain extenders, they induce a smaller phase separation than diamine.[15] Here, PUs were synthesized from PTMO 1000/IPDI/BD in the respective molar ratios of 1/2/1. PUs synthesized with PDMS have generally poorer mechanical properties than traditional PUs.[16] It has been found that concentrations of PDMS higher than 2 wt% (often used in block and graft copolymer studies) invariably lead to a significant reduction in mechanical properties of PUs.[17,18] Only small amounts of PDMS must be added to maintain the bulk properties of the system. A percentage of 2 wt% was thus chosen. A PDMS of high molecular mass (2500 g·mol^{-1}) was selected to favor the crystallization of the soft sequences (SS).[19] Two procedures for incorporating PDMS into urethanes were studied, depending on whether PDMS was introduced in the first step or in the second step.

Sample designation and their composition data are listed in Table 2. Several PUs with the same formulation have been prepared and characterized. The reproducibility of

Table 2. Chemical compositions of various PUs (❶ and s❷ for respective addition of PDMS at the first and second stage of polymerization).

| Designation | $\overline{M_n}$ (g·mol^{-1}) PTMO/PDMS | Molar ratio | | Segment content | |
		PTMO/IPDI	BD/PDMS	Soft (SS) (wt%)	Hard (HS) (wt%)
PU 1/2/1	1000/0	1/2	1/0	63	37
PU-PDMS❶	1000/2500	1/2	0.9876/0.0124	63.7	36.3
PU-PDMS❷	1000/2500	1/2	0.9876/0.0124	63.7	36.3
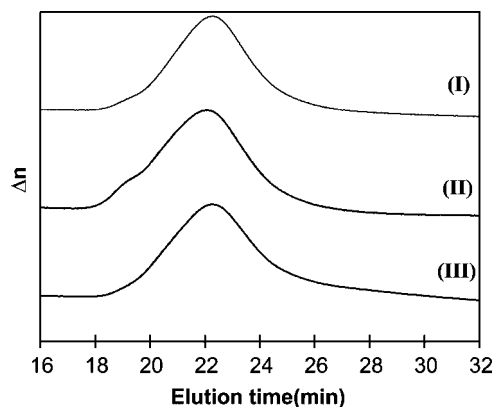
Figure 2. SEC chromatograms of PUs with and without PDMS: (I) PU 1/2/1, (II) PU-PDMS❶, (III) PU-PDMS❷.

the results obtained from these formulations was total. Only the results for one of them have been reported in this work.
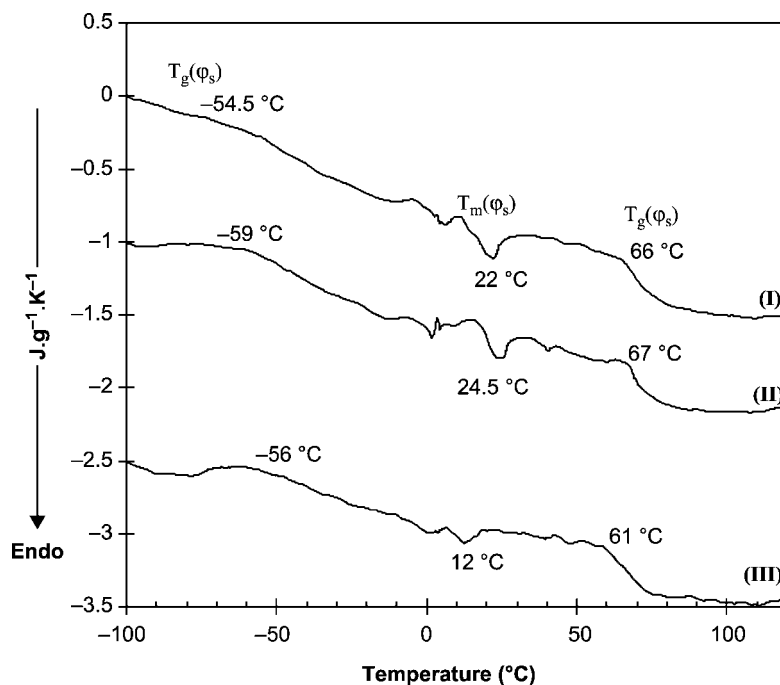
Characterization by SEC

The SEC chromatograms are shown in Fig. 2. The results of the molar mass measurements are listed in Table 3. There is no standard for the siloxane-containing urethane copolymers: the conventional polystyrene standards are used for the calibration of the molecular weight in terms of elution time or volume to indicate the relative $\overline{M_n}$ and $\overline{M_w}$ values for these PDMS-PU polymers. Relative standard deviations for molecular weight values were evaluated to 10%.

The addition of the PDMS in the second step of synthesis (i.e., at the same time as BD) involves an exceptionally high molecular dispersity (I_p). In addition, the corresponding PU (PU–PDMS❷) offers a relatively weak $\overline{M_n}$ value, even if the molar mass at the maximum of the peak is 109290 g·mol^{-1} and is comparable with these of PU-PDMS❶ and PU 1/2/1. The simultaneous introduction of the PDMS with the chain extender consequently seems to disturb the growth of the PU chains. Conversely, the

Table 3. Evaluation of the number- and the weight-average molar masses ($\overline{M_n}$ and $\overline{M_w}$), the molecular weight at the maximum peak ($\overline{M_p}$) and the polydispersity (I_p) calculated with SEC data for various PUs.

Polymer	$\overline{M_n}$ (g·mol^{-1})	$\overline{M_w}$ (g·mol^{-1})	M_p (g·mol^{-1})	I_p
PU 1/2/1	60100	132200	108000	2.2
PU-PDMS❶	67700	147900	132100	2.2
PU-PDMS❷	24800	117400	109300	4.7

Figure 3. DSC thermograms of PUs with and without PDMS: (I) PU 1/2/1, (II) PU-PDMS❶, (III) PU-PDMS❷.

addition of PDMS in the first step of synthesis (PU-PDMS❶) reveals a shoulder on the chromatogram for retention times corresponding to high molar masses. To explain this result, one can suggest a good introduction of PDMS within the soft chains, which leads to an increase of the polymer chain lengths. The kinetic study has shown that the reactivity of PDMS towards IPDI was largely higher than that of PTMO. We can thus expect a larger number of PDMS molecules in the medium of soft chains when they are added with PTMO; on the contrary the addition of PDMS with the chain extender probably gives a more random distribution.

Table 4. Characteristics of various PUs obtained by DSC.

Polymer	$T_g(\varphi_S)$ (°C)	ΔT_0^a (°C)	$T_m(\varphi_S)$ (°C)	$\Delta H_m(\varphi_S)$ (J·g^{-1})	$T_g(\varphi_H)$ (°C)
PU 1/2/1	−54.5	43	22	2	66
PU-PDMS❶	−59	38.5	24.5	1.5	67
PU-PDMS❷	−56	41.5	12	0.6	61

$^a \Delta T_0 = T_g(\varphi_S) - T_{g0}(ss)$, where ss = soft segment, φ_S = soft phase, φ_H = hard phase, and $T_{g0}(ss) = T_g$ of pure SS.

Characterization by DSC

The DSC thermograms of the PUs are illustrated in Fig. 3. The absence of the melting peak specific to the hard domains was noted. This is attributed to the asymmetry of the IPDI molecule. The presence of an endothermic melting peak, characteristic of the soft phase (φ_S) was observed. The glass transition temperature of the hard domain ($T_g(\varphi_H)$) could be detected. The DSC results of the PUs are summarized in Table 4. The formulations containing PDMS 2500 presents a behavior similar to the model system corresponding to PU 1/2/1. In the case of PU-PDMS❷ a lower $T_g(\varphi_H)$ was recorded: 61°C against 67 and 66°C for PU-PDMS❶ and PU 1/2/1. In addition PU-PDMS❷ reveals a melting point of soft segments (SS) ($T_m(\varphi_S) = 12$°C) clearly lower than the other two PUs for which $T_m(\varphi_S)$ exceed 20°C. The enthalpy of melting $\Delta H_m(\varphi_S)$ is relatively weak (0.6 J·g^{-1}). This suggests that PU-PDMS❷ leads to a lower organization and a smaller domain size of the soft segments. The literature mentions the inaptitude to crystallize for PU formulated with PDMS as the only macrodiol.[16] When the polycondensation reaction is carried out in bulk, it is mainly due to a premature phase separation, which gives an heterogeneous composition. In this work, when PDMS is added with the chain extender it would provide nothing, but it would reinforce the incompatibility of the chain extender towards IPDI.

The DSC curves exhibited a shift of the melting point from 22°C for the basic PU formulation (PU 1/2/1) to 24.5°C for PU-PDMS❶. This tends to prove that the good incorporation of PDMS within the soft chains, already suggested by the SEC results, involves a better phase separation, even if the values of heat of fusion ($\Delta H_m(\varphi_S)$) show that the presence of PDMS decreases crystallization. This confirms that PDMS is an apolar macrodiol and cannot develop hydrogen bonds with the hard sequences, implying a greater phase separation.[19] We can also notice a decrease of the glass transition temperature of the soft phase $T_g(\varphi_S)$ which loses approximately 4 to 5°C, whereas T_g of the rigid phase is slightly higher compared with the T_g of PU 1/2/1: even if these results are within experimental error, they are indicative of improved phase separation for PU-PDMS❶.

*Table 5.* Dynamic mechanical properties of various PUs.

Polymer	(tan δ)$_{max}$			Decrease of log G′^{a}	
	$T_g(\varphi_S)_{[\tan \delta]}$ (°C)	Value	$\Delta T_{\tan \delta - DSC}$^{b} (°C)	$T_g(\varphi_S)_{[\text{Log }G']}$ (°C)	$\Delta T_{\text{Log }G' - DSC}$^{c} (°C)
PU 1/2/1	3.5	0.78	58	−19	35.5
PU-PDMS❶	3	0.74	62	−19	35
PU-PDMS❷	5	0.88	61	−21	35

^{a} $T_g(\varphi_S)_{[\text{Log }G']}$: glass transition of the soft phase (onset, midpoint, end-set).
^{b} $\Delta T_{\tan \delta - DSC}$, and
^{c} $\Delta T_{\text{Log }G' - DSC}$: difference between the glass transition temperature detected at the maximum of tan δ($T_g(\varphi_S)_{[\tan \delta]}$) and at the decrease of Log G′($T_g(\varphi_S)_{[\text{Log }G']}$) compared to the temperature obtained from DSC ($T_g(\varphi_S)$).
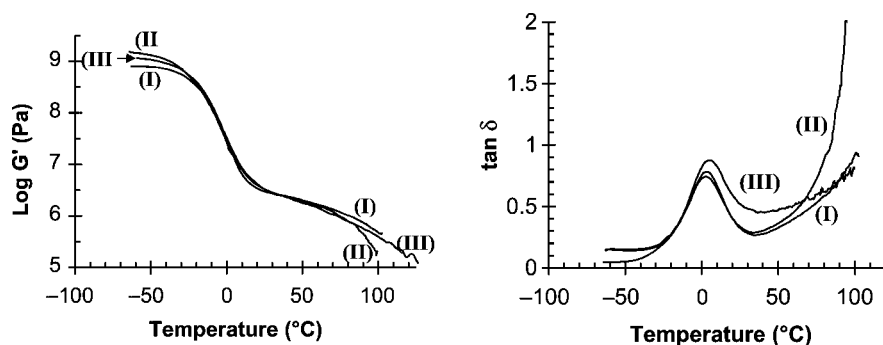
Figure 4. The evolution of elastic modulus (G′) and loss tangent (tan δ) as a function of temperature for PUs with and without PDMS: (I) PU 1/2/1, (II) PU-PDMS❶, (III) PU-PDMS❷.

Characterization by DMTA

Table 5 summarizes all the thermomechanical characteristics shown for the different synthesized PUs. It is divided into two parts: each one of them refers to the respective detection of the maximum of loss tangent (tan δ) and the decrease of the elastic modulus (G′) due to the glass transition of the soft phase. The transition relative to the hard segments is not observable with this mean of characterization, contrarily to DSC measurements.

The thermomechanical analysis does not enable us to detect notable differences and to come to a conclusion on the effect of the addition of the PDMS in our basic formulation PU 1/2/1 (Fig. 4).

The $T_g(\varphi_S)$ estimated from DMTA results shifted to higher temperatures compared to DSC results: this is due to the dynamical nature of the tests. It is worth noting that the difference is identical for the three formulations whether the glass transition is detected at the maximum of tan δ ($\Delta T_{\tan\delta-DSC} = 35°C$) or at the falling of G′ ($\Delta T_{\text{Log } G'-DSC} \approx 60°C$). DMTA results corroborate the DSC ones.

Table 6. Static mechanical characteristics for PUs calculated from 5 tests, reported with the corresponding standard derivations.
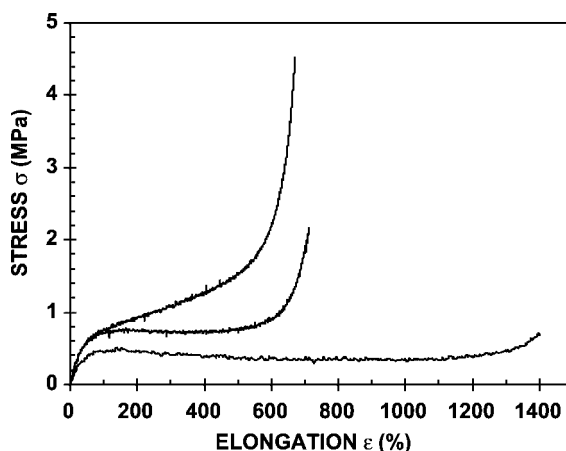
Polymer	Hard segment (wt%)	E_0[a] (MPa)	σ_b[b] (MPa)	ε_b[c] (%)
PU 1/2/1	37	2.0 ± 0.2	2.4 ± 0.3	671 ± 5
PU-PDMS❶	36	2.1 ± 0.1	2.2 ± 0.4	683 ± 21
PU-PDMS❷	36	1.1 ± 0.15	0.72 ± 0.03[d]	1400 ± 180

[a] E_0 = initial Young's modulus.
[b] σ_b = tensile stress at break.
[c] ε_b = ultimate elongation.
[d] When break is not observed.

Figure 5. Typical stress–elongation curves of PUs with and without PDMS at ambient temperature: (I) PU 1/2/1, (II) PU-PDMS❶ , (III) PU-PDMS❷.

Characterization in Uniaxial Tensile Testing

The tensile testing of our samples was carried out in static mode. The results (modulus at 0% elongation (E_0), stress at break (σ_r) and ultimate elongation (ε_r) are reported in Table 6 and the curves are shown in Fig. 5.

In Fig. 5, one can clearly see the reduction of the mechanical properties due to the incorporation of the PDMS. The extreme case is illustrated by PU-PDMS❷ with an initial modulus (E_0) decreased by half and a very low σ_R. On the other hand, it gains in elasticity and has an elongation at break higher than 1400%. In SEC a weak $\overline{M_n}$ value was found for this polymer; this would justify a loss in cohesion of material as well as the decrease in the modulus E_0.

PU-PDMS❶ has an initial static modulus E_0 comparable with that of basic PU. The difference results in a reduction of the hardening of material due to a less easy orientation of the chains in the direction of the stretching.

CONCLUSION

Polyurethanes (PU) containing poly(tetramethylene oxide) (PTMO), isophorone diisocyanate (IPDI) and 1,4-butanediol (BD) in respective molar proportions 1/2/1 have been synthesized and 2 wt% of hydroxy-terminated poly(dimethylsiloxane) (PDMS) was incorporated in these formulations. The main differences with the majority of studies reported in literature are that a mixture of polyols in PUs formulations is used and the synthesis was carried out in bulk, without catalyst.

The kinetic study showed that PDMS is more reactive than PTMO. However this difference can be diminish by the addition of a catalyst.

Even in a small quantity (2 wt%), the PDMS is likely to modify the properties of PU. Two procedures for incorporating PDMS were studied. The characterization of the PU-PDMS polymers by SEC, DSC and in tensile testing allow us to see morphological differences between both of them. When added at the second step with BD, siloxane causes a significant polydispersity of the chains and a consequent reduction in the $\overline{M}_n$ value. The mechanical properties in static mode (initial modulus, stress and elongation at break) decrease. When it is introduced at the first step of the synthesis with PTMO, the result is less dramatic; PDMS seems to be better incorporated within the PU chains.

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