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Coarsening of nanodomains by reorganization of polysiloxane segments at high temperature in polyurethane / α , ω -aminopropyl polydimethylsiloxane blends.

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ABSTRACT

The reaction in bulk at high temperature of α,ω -aminopropyl oligodimethylsiloxane and thermoplastic polyurethane (TPU) allowed observing interesting behaviour. Mixing at 200°C first involved dissociation of urethanes and splitting of polyurethane chains followed by reaction of the released isocyanates with amino end-groups of the oligosiloxane. At this stage, a copolymer was formed which morphology consisted of a very fine dispersion of the polysiloxane domains at the nanoscale (20 nm) with a narrow size dispersity. The polymer blend was perfectly transparent. Increasing the reaction time resulted in a significant coarsening of the morphology and a consequent loss of transparency. The reason for such a morphology evolution has been elucidated. The progressive formation of alkyl-alkyl urea linkages at the expense of aryl-alkyl bonds obtained earlier in the process caused an increase in the average number of successive polydimethylsiloxane (PDMS) blocks that organized in larger domains. The average number of consecutive polysiloxane segments was found to evolve from ~1.5 in the first 10-15 minutes to a value of 3-5 at the end of the reactive process.

Keywords: polyurethanes, polysiloxanes, melt reaction, copolymer.

1. Introduction

A large number of works is dedicated to the association of polyurethanes with polysiloxanes, either in simple blends prepared by a classical melt mixing technique, or using polydimethylsiloxane (PDMS) oligomers as reactive precursors in the synthesis of segmented polyurethane or polyurethane-urea copolymers[1-3]. The main objective is usually to take advantage of the specific surface properties linked to the introduction of silicone known to be highly hydrophobic. The applications are materials with minimal biological adhesion used in medical devices where the antithrombogenicity of the surface is needed (artificial heart or vascular grafts, implants...), or in coatings where the settlement of marine organism[4] must be inhibited. Also, better hydrolytic stability can be achieved in the presence of silicone, as well as flame retardancy with a halogen-free component. Finally, gas permeation can be tuned depending on the structure of the material[5,6].

Copolymers are usually obtained from the reaction of hydroxyalkyl- or aminoalkyl-terminated oligosiloxanes with diisocyanates and diols. The reaction is most often carried out in solution in mixtures of solvents that must be carefully selected to maintain the homogeneity of the reactive medium. Indeed, the large solubility difference between the non-polar silicone and the highly polar urethane segments tends to induce a macrophase separation. Therefore the mechanical properties obtained when using only PDMS as soft segment are often rather poor, also because of possible end-group instabilities of the hydroxy-terminated PDMS oligomers. In order to improve the miscibility of the reactive systems and the material final properties, the use of mixtures of PDMS oligomers with a second macrodiol such as poly(propylene oxide), poly(tetramethylene oxide) or preferably poly(hexamethylene oxide) has been recommended by several authors[7-11].

The particular surface properties of poly(urethane-urea) copolymers containing silicone are obtained through the segregation of incompatible and less polar soft silicone domains toward the surface to minimize the interfacial tension with air[12,13]. The bulk compositional features of the copolymers are less understood. A complex microphase separation of PDMS segments from a mixture between a second soft segment (polyoxypropylene) and the hard segments was observed but not clearly explained[14]. Actually, the immiscibility of the three types of segments should involve a ternary structure but this point was not always elucidated in the literature. Recently, Hernandez *et al* [9] investigated the microstructural organization of PDMS-based polyurethanes synthesized from mixed macrodiols, especially by SAXS and DMA; they found that the polyurethanes under study indeed organized into three phases: hard domains, silicone domains, and a mixed phase composed of the second macrodiol, PDMS end-group segments, and dissolved hard segment sequences. In polyurethanes, the size of the hard segment domains is often estimated to be 3-5 nm[15-17]. On the other hand, the size of the silicone-rich domains varies from a few tens of nanometers to more than 100 nm depending on the PDMS content and molar mass[18,19].

By contrast to the typical solution method usually employed in the literature, here the copolymers will be synthesized in the melt state starting from a thermoplastic polyurethane and amino-functional oligodimethylsiloxanes. More precisely, this work focuses on the reactions between the polyurethane and α,ω -aminopropyl polydimethylsiloxane at high temperature (200°C). A special emphasis is put on the evolution of the morphology of the copolymer during reactive processing. For comparison, blends obtained by mixing the same TPU with a commercial polydimethylsiloxane-urea copolymer have been prepared and characterized.

2. Experimental

2.1. Materials

The thermoplastic polyurethane (TPU) elastomer was a commercial polyester-based TPU, Elastollan 685A (named E685), kindly supplied by BASF, with poly(butylene adipate) soft segments and hard segments based on 4,4'-diphenylmethane diisocyanate (MDI), and 1,4-butanediol (BDO) (Figure 1). The α,ω -aminopropyl oligosiloxanes were supplied by Wacker Chemie. Three different molar masses were used referenced respectively as PDMS15D, PDMS40D and PDMS130D. They were all liquid at room temperature. A thermoplastic silicone elastomer, Geniomer 80 (G80), given by Wacker was also used. It was a polydimethylsiloxane-urea copolymer obtained by the stoichiometric reaction of an α,ω -aminopropyl polydimethylsiloxane with $\bar{M}_n=2.75 \cdot 10^3$ g/mol (^1H NMR determination) with isophorone diisocyanate (IPDI) (Table 1, Figure 1). The molar masses of G80 and E685 are also given in Table 1.

2.2. Blending method

The thermoplastic polyurethane was dried at 90°C for at least 4 hours. Geniomer 80 was dried under vacuum (200 mbar) at 30°C for at least 4 hours. PDMS oligomers were dried during 9 hours at 90°C. The extrusion was performed in a DSM 15 cm³ twin-screw mini-extruder. The extruder was charged with 13.5 g of materials corresponding to the maximum volume (15 cm³) of the chamber.

2.2.1. Blends of polyurethane E685 with α,ω -aminopropyl polydimethylsiloxane oligomers.

Half of the calculated amount of TPU pellets was charged into the mini-extruder heated up to 200 °C at a screw speed of 100 rotations per minute. The mini-extruder drive was then stopped,

the silicone building blocks were injected into the chamber using a syringe, and the second half of the pellets was charged. Samples were extruded after different mixing times.

2.2.2. Blends of polyurethane E685 with polydimethylsiloxane-urea copolymer G80

The thermoplastic silicone and TPU pellets were dry blended and then fed at the same time in the extruder. In this case, the residence time in the extruder was set to 10 minutes.

The extrudates were always immediately quenched in cold water at the exit of the die.

2.3. Nuclear Magnetic Resonance Spectroscopy (NMR)

High-resolution liquid NMR spectroscopy was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for ^1H . Spectra were obtained with a 5 mm- QNP probe at 298K or 323K. Deuterated tetrahydrofuran was used as solvent. Chemical shifts values are given in ppm with reference to internal tetramethylsilane.

2.4. Transmission Electron Microscopy (TEM)

Transmission electron microscopy analyses were carried out at the “Centre Technologique des Microstructures de l’Université Claude Bernard Lyon 1” on a Philips CM120 microscope operating at 80 kV. The samples were ultra-microtomed at low temperature (-100°C) by a LEICA ultra-microtom, to have thin sections with a thickness around 80 nm.

2.5. Size Exclusion Chromatography (SEC)

The blends were analyzed by SEC using a Viscotek device equipped with a Viscotek VE 1121 pump and using 3 Waters columns HR 5E. The eluent used was tetrahydrofuran (THF) at a flow rate of 1 mL/min. The detectors included differential refractometer Viscotek VE3580, and a Viscotek Dual T60 detector (combining a right angle light scattering detector and a

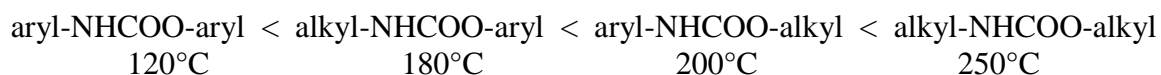
viscosimeter). Low molar mass components were analyzed using special columns (Viscotek G3000H and G2000H) with refractive index detector. Average molar masses were calculated using 3 detectors calculation method. As amino-terminated oligodimethylsiloxane could not be directly detected and analyzed, both because they partially adsorb on the columns and because their refraction index is quite close to that of THF, they were initially modified using p-tolylisocyanate in THF solution. The same method was used for the reactive blends whenever these oligomers could be present.

3. Results and discussion

3.1. Polyurethane/ α , ω -aminopropyl oligosiloxane blends

3.1.1. Reactive process

The mixing process of the polyurethane with α , ω -aminopropyl oligosiloxane at high temperature does not consist only in simple mixing but is likely to involve several chemical reactions. First, the thermal reversibility of urethane bond above a temperature depending on its chemical structure (usually above 150-170°C) is indeed well-known[20,21] and was shown for example to induce a strong broadening of the molar mass distribution when heating an initially monodisperse polyurethane[22]. The stability scale for urethane bonds is given as follows:



This reversibility phenomenon occurs under classical TPU processing conditions, although it was shown from theoretical kinetics calculations that only a tiny fraction of the urethane bonds were actually split, for example about 1% at 235°C [23]; however a classical commercial TPU typically bears 3-400 urethanes per chain and even such a small proportion of bond scission can have non negligible consequences on the average molar mass.

Moreover, if the TPU is processed in the presence of amino-terminated oligomers, depending on the experimental conditions various NCO/OH or NCO/NH₂ recombinations can occur, and the formation of more or less randomized copolymers could therefore be expected. In the present work at temperatures above 170 °C, urethanes can split into isocyanate-terminated and hydroxyl-terminated chains. The reaction of isocyanates with amino groups of the oligosiloxane is favored rather than recombination with hydroxyl-terminated chains. This assumption is supported by a quite complete study involving model urethanes and various reactive monofunctional compounds by Lu *et al* [24] where the authors demonstrated that among all used functions, the amines (primary or secondary) were the most suitable to allow reactive compatibilization of TPUs with other functional but non miscible polymers. Therefore, under the used mixing conditions the formation of urethane-polysiloxane block or segmented copolymers is expected with a final structure depending on the composition of the blend (Scheme 1).

Because of such differences in reaction rates and stoichiometric imbalance, some excess of free hydroxyl groups should remain in the final blends, whereas amino-building blocks are expected to be ultimately entirely incorporated inside the chains, leaving no remaining NH₂ groups. Ideally, the final amount of released OH groups should be equal to the initial amount of NH₂ groups. The reaction of amino groups with isocyanate being very fast, the polysiloxane blocks should be rapidly incorporated along the TPU chains through the formation of aryl-alkyl urea groups (Scheme 1). Finally, the introduction of low molar mass silicone blocks and the resulting chain rearrangements, together with possible chain scissions during extrusion [23] should result in an overall decrease in the average molar mass of the polymer blends compared to the neat TPUs, and this decrease should be even sharper when higher amounts of low molar mass species are initially added. This hypothesis was indeed confirmed experimentally by size exclusion chromatography (see below, § 3.2)

The axial force of the extruder screw is related to the viscosity of the molten mixture, thus it gives qualitative indications about mixing and reaction progress (Figure 2a). The injection of liquid oligosiloxanes is done at time $t=0$. After injection, a lubrication phenomenon induced by the addition of low viscosity immiscible silicone to the high molar mass viscous polyurethane leads to a drastic drop of the screw force. Afterwards, the force rises strongly because of two competing phenomena, physical dispersion of the liquid silicone and reaction of the oligomer amino end-groups with reversible urethane bonds. A maximum force is reached once the amino-isocyanate reaction is completed. Samples of the blend were taken off after 3 minutes mixing and then 2, 12 and 17 minutes after reaching the maximum of the force. The extrudates appearance is very different depending on the time of sample withdrawal. As shown in Figure 2, with PDMS40D, the first sample was totally opaque while the second was perfectly transparent. Then this transparency is progressively lost by increasing the mixing time (the third sample is translucent), ending with a fully opaque blend. Explanations for such a behavior will be given in the next section devoted to the morphology analysis of the blends.

As it is classically done for reactive processing in a batch mixer, the apparent rate of reaction between the silicone amino end-groups and the TPU can be roughly estimated from the evolution of the force recorded on the extruder screws. The strong increase in the force enables to set approximately the completion of the reaction and the end of blend homogenization. Using this criterion it was found that the reaction time for total conversion was directly related to the proportion of oligosiloxane and to a lesser extent to its viscosity (see supplementary data). As an example, when the weight fraction of oligosiloxane increases, the screw force maximum is shifted to longer times. This feature is obviously not related to differences in the actual kinetics of the amine-isocyanate reaction, but rather to the influence of the mixing process on the reaction. Indeed, the amine-isocyanate reaction has to occur at the TPU-silicone interface. At the early stage of the mixing process, the silicone is dispersed in the shape of large liquid drops in

the TPU matrix. As soon as the reaction proceeds, a copolymer is formed and located at the interface that has to be continuously renewed for the reaction to proceed. This mechanism takes time, which explains that higher reaction times are observed when for the same PDMS oligomer the weight fraction of silicone increases (although the initial NH_2 concentration also increases). In contrast no clear variation was observed when using equal weight fractions of oligomers with increasing molar mass (i.e. decreasing NH_2 concentration). The influence of the viscosity of the silicone is less clear and quite similar apparent reaction rates are observed depending on the molar mass of the used oligomers(see supplementary data).

3.1.2. Morphology and reactions

As a preliminary comment, it is interesting to notice that the liquid α,ω -aminopropyl oligosiloxane is highly immiscible and incompatible with the E685 polyurethane as can be seen in Figure 3 where the micrograph of a blend prepared in solution is presented. In this blend prepared at ambient temperature, no chemical reactions occurred between the polyurethane and the silicone, and the morphology is coarse with silicone domains of 2-10 μm diameter, typical of an immiscible mixture where interfacial interactions are very weak.

When the blend is prepared at high temperature, the extrudate collected after only 3 minutes mixing is highly inhomogeneous. It contains unreacted liquid silicone badly dispersed in the melt. These domains appear as white holes in the polymer slice cut for microscopy (Figure 2A). They are however quite small (0.5-2 μm) and significantly smaller than those of the blend prepared at ambient temperature. This demonstrates that even at this short reaction time some copolymer is already formed at the interface and is compatibilizing the dispersion. The material also contains very small dark domains visible on the TEM images (zoom in Figure 2A) that could be composed of reacted polysiloxane finally dispersed.

The second sample, taken after 12 minutes mixing, just after the maximum of screw force is shown in Figure 2B. Very small spherical silicone domains of about 20 nm diameter are then

present in the TEM image, they appear throughout the sample and larger diameter structures are no longer visible. The distribution of the diameters is very narrow. This morphology is related to the total reaction of the α,ω -aminopropyl oligosiloxanes leading to their complete insertion into the polyurethane macromolecules as will be demonstrated later. This very fine morphology explains that the extrudate is perfectly transparent since such small heterogeneities do not diffuse visible light. However, this morphology is not stable as seen in Figure 2C and D. The nanodomains of silicone coarsen significantly upon longer mixing time (22 and 27 minutes). This coarsening is not caused by physical coalescence of droplets since they are no longer composed of individualized silicon chains, but rather of PDMS segments from the PU-co-PDMS copolymer. The coarsening is thought to be linked to a change in the structure of the macromolecules and more precisely to an increase in the average length of the PDMS blocks. At this point, it is necessary to get a deeper insight into all the different chemical reactions that are likely to occur in the TPU/silicone reactive medium.

- Formation of aryl-alkyl urea

As discussed before, the amine and the urethane can react directly, or the urethane can split into alcohol and isocyanate. The latter is able to react very rapidly with the amine and thus form an aryl-alkyl urea during the early stages of the process[24]. To assert this comment, Figure 4 depicts the ^1H NMR spectrum of the blend of E685 with 10wt% PDMS40D after 12 minutes mixing. A new signal labeled “b” from $\text{CH}_2\text{NH}(\text{C}=\text{O})$ protons clearly shows the formation of the aryl-alkyl urea while the signal labeled “a” from CH_2OH protons reflects the formation of hydroxyl-terminated TPU. In parallel, the peak of the amine end-groups of oligosiloxane decreases to reach a non detectable value. The conversion of these amine groups is already complete after 12 minutes of reaction with 10 wt% PDMS40D and almost complete after 10 minutes with 10wt% PDMS15D (Table 2). These mixing times are in good agreement with those

estimated from the maximum force of the screws observed at 10 and 7 minutes for PDMS40D and PDMS15D, respectively.

- Formation of alkyl-alkyl urea

The formation of TPU/PDMS aryl-alkyl urea is not the only chemical reaction that can be encountered. By reacting their diurethane model with an aliphatic primary amine, Lu et al. have shown that after longer mixing times, alkyl-alkyl urea were formed and aryl-aryl urea were formed even later[24]. Those functions come from the cleavage of unsymmetrical urea groups into alkyl isocyanate and primary aromatic amine. The reaction of the former with primary alkyl amine borne by the oligosiloxane leads to alkyl-alkyl urea while reaction of aromatic amine with urethane functions gives aryl-aryl urea. The reactions are outlined in Scheme 2.

As evidenced by ^1H NMR, under our conditions, a low proportion of alkyl-alkyl urea is formed during the early stages of the process (signal labeled “c” from $\text{CH}_2\text{NH}(\text{C}=\text{O})$ protons) (Figure 4) and the concentration increases as the reaction proceeds (Table 2).

In the material, PDMS segments can be ended with three different functions (amine, aryl-alkyl urea and alkyl-alkyl urea, see Scheme 2) which ratio depends on the mixing time. These ratios are given in Table 2 for several blends as a function of mixing time. They were calculated by dividing the integral values of signals at 2.60 ppm (CH_2NH_2 of residual amine), 3.15 ppm ($\text{CH}_2\text{NH}(\text{C}=\text{O})$ of aryl-alkyl urea) and 3.06 ppm $\text{CH}_2\text{NH}(\text{C}=\text{O})$ of alkyl-alkyl urea) by the integral value of signal at 0.59 ppm (CH_2 groups linked to PDMS).

The overall contribution of polysiloxane terminal groups does not always complete 100% with respect to the signal at 0.59 ppm, which means that other functions coming from side reactions of amines should coexist in the blend. One small signal is actually observed at 10.9 ppm and could suggest the formation of some allophanate functions through the addition of aromatic isocyanate on TPU urethane groups. The NMR analysis of such allophanate functions

have already been reported: their NH NMR signals were observed at 10.85 ppm in acetone-d₆ solution[25] and 10.65 ppm in DMSO-d₆ [26].

- Formation of aryl-aryl urea

Concerning aryl-aryl urea functions, their formation is difficult to confirm as their NH NMR peaks are expected to be very close to the NH urethane signals. Nevertheless three different couples of signals were observed in the region of aromatic protons for all the sampled blends. As the main signals at 7.34 ppm and 7.02 ppm are attributed to protons of aromatic ring bearing urethane functions, those slightly shifted to higher fields, at 7.28 ppm and 6.96ppm respectively, were assumed to correspond to aromatic protons close to aryl-alkyl urea groups. The smaller signals at 6.81 ppm and 6.46 ppm could then belong to aromatic rings of aryl-aryl urea functions. These signals were present in all the spectra of sampled blends. They are shown in the ¹H NMR spectrum of the 10wt% PDMS15D blend after 25 minutes mixing (Figure 5).

The evolution of the proportion of amino groups from the oligosiloxane, aryl-alkyl groups and alkyl-alkyl groups of the TPU-co-PDMS copolymer are collected in Table 2 and the example of E685/PDMS15D 90/10 wt% blend processed at 200°C is depicted in Figure 6. To summarize briefly, the amino groups of the PDMS oligomers react rapidly with the isocyanates issued from the splitting of the urethanes and form aryl-alkyl ureas. Then alkyl-alkyl ureas are formed from the splitting of the aryl-alkyl groups.

These chemical observations now allow to go back over macromolecular structure, and its consequences on the morphology evolution displayed in Figure 2. The insertion of polysiloxane moieties into TPU chains is produced very early in the process through the reaction involving urethane groups and amino-terminated siloxane. Thus, regarding the large excess of urethane links compared to available amine, most of the siloxane units are initially individualized along the chain as depicted schematically in Scheme 3. As a consequence these

units segregate in the shape of nanosized spherical domains (about 20 nm diameter, see Figure 2B). Later on, increasing amounts of alkyl-alkyl urea groups are formed. Each of them implies the presence of two consecutive polysiloxane segments in the copolymer chain, and thus the formation of alkyl-alkyl ureas leads to an increase in the average length of the PDMS blocks in this copolymer, as shown in Scheme 3. These blocks can then segregate in the shape of larger domains (about 100 nm or more depending on the composition of blend, see Figure 2C).

The NMR data collected and summarized in Table 2 have been used to evaluate an average number of consecutive polysiloxane segments, N . Indeed the proportion of aryl-alkyl and alkyl-alkyl ureas brings this information if we neglect the side reactions and consider the situation where there is no residual amine. N is expressed as:

$$N = 1 + \frac{2 \phi_{\text{alkyl-alkyl}}}{\phi_{\text{aryl-alkyl}}} \quad (1)$$

Where $\phi_{\text{aryl-alkyl}}$ and $\phi_{\text{alkyl-alkyl}}$ are the molar ratio of respectively aryl-alkyl and alkyl-alkyl groups relative to the total (aryl-alkyl + alkyl-alkyl).

The average number of concomitant polysiloxane segments reaches values around 3-5 at the end of the process (Table 2).

3.2. Polyurethane/ thermoplastic polydimethylsiloxane-urea copolymer blends

Finally, a blend of the same polyurethane, E685, with a high molar mass thermoplastic silicone has been extruded to be compared with the previous E685/amino-terminated PDMS blends. The thermoplastic silicone is a polydimethylsiloxane-urea copolymer (Geniomer G80) obtained by the stoichiometric reaction of an α,ω -aminopropyl polydimethylsiloxane with isophorone diisocyanate (Figure 1). It was chosen because its structure is very similar to that hypothesized for the PDMS segments.

The morphology of the E685/Geniomer80 90/10 w% blend depicted in Figure 7a is showing spherical silicone domains with 50 to 250 nm diameter, which is actually very small for an immiscible polymer blend. By comparing Figure 7a with Figure 7b one can observe that the morphology of the E685/Geniomer 80 is quite similar to that obtained by blending during 24 minutes the large molar mass α,ω -aminopropyl oligosiloxane, PDMS130D, with E685.

Such a fine structure is linked to the reactions that possibly occur during the mixing process (Scheme 4). Under the used experimental conditions, the urethane and urea linkages from respectively polyurethane and PDMS-urea chains once again are reversible and prone to dissociation releasing isocyanate, alcohol and amine end-groups that can further react to produce block and segmented copolymers. Such copolymers are well known to compatibilize immiscible blends and stabilize their morphology. The compatibilization seems to be highly efficient since very small droplets of silicone are dispersed in the TPU matrix. Those blends of TPU and silicone thermoplastic elastomer G80 were investigated by NMR.

Neither ^1H nor ^{13}C NMR spectra of the TPU / G80 blend (20 wt% of G80) exhibit significant signals suggesting the formation of new urea or urethane groups; e.g. no new carbonyl signal from urethane groups could be detected in the ^{13}C spectra. From the ^1H spectrum it is difficult to show the formation of new alkyl-alkyl urea functions since they are already present in the spectrum of G80. Moreover the amount of reactive groups from Geniomer 80 that could react with the TPU is low. When 20 wt% of Geniomer 80 is used, the ratio of the total amount of isocyanate from TPU (MDI) to the amount of isocyanate from G80 (IPDI) is around 10:1. If only some part of the urethane and especially of the urea groups split during extrusion and give free reactive groups[23], such a low content does not allow to confirm or to evaluate the extent of the reactions by means of NMR. An indirect proof of the formation of TPU-PDMS copolymer can nevertheless be found with the presence in the ^1H spectrum of the TPU/G80 blend of a multiplet at 3.5 ppm from hydroxyl end groups ($-\text{CH}_2-\text{CH}_2-\text{OH}$), this signal is

analogous to the one observed for the TPU/ α,ω -aminopropyl oligosiloxane blends. These end groups can only result from the splitting of urethane bonds and the free isocyanate was therefore able to recombine with some amine function originating from G80.

Attempts were finally done to monitor the extent of the reaction by means of size exclusion chromatography, SEC, both with oligosiloxanes and with the thermoplastic silicone elastomer. Initially one aim of the experiment was, especially in the first case, to detect if any non-reacted amino blocks remained in the final blends. But for mixtures with small amounts of oligomers, and even though the blends were modified with p-tolylisocyanate, it was in fact very difficult to detect the peak of these amino-blocks, and therefore SEC finally could not provide reliable data for the precise determination of remaining species. However it gave other valuable information. Using the amino-terminated oligomers, the main peak of the TPU globally shifted towards lower molar masses, which was another proof that a reaction occurred (scissions of TPU chains by low molar mass silicone blocks and rearrangements leading to a decrease in the overall average molar mass). As shown in Figure 8, this was not observed with the thermoplastic silicone elastomer, for which only a slight increase in the average molar mass was noted at the very beginning (also observed with the oligomers), followed by a rather constant value of this molar mass. As the reaction proceeds, and given that the TPU and the elastomer G80 have initially comparable molar masses, the rearrangement reactions induce no noticeable change in these M_w values. Such result proves that the decrease in molar mass observed with the oligomers cannot be attributed to some thermal degradation, but definitely results from rearrangement reactions. If thermal degradation occurred, it would also be observed for the blends with G80 that are produced exactly under the same conditions, and it would result in a decrease in the overall molar mass in this case as well.

4. Conclusion

Generally, PDMS/TPU copolymers are obtained via a reaction involving TPU precursors and functional PDMS oligomers and most often the reaction is done in solution at moderate temperature. Here α,ω -aminopropyl polydimethylsiloxane (PDMS) and thermoplastic polyurethane (TPU) have been reacted in bulk and the elevated temperature allows observing specific behaviour. At 200°C the splitting of the urethane group of the TPU is releasing hydroxyl and isocyanate terminated TPU chains. The splitting is followed by the fast reaction of the amino-siloxane with the isocyanate. This reaction forms aryl-alkyl ureas and promotes the insertion of individual PDMS segments inside the TPU chains, forming TPU-co-PDMS copolymer with a very fine morphology (~20nm). However the morphology is not stable and coarsening is observed for longer reaction times. This morphology evolution had to be explained. Actually, after the formation of the aryl-alkyl ureas several reactions proceed. One is the cleavage of unsymmetrical aryl-alkyl urea groups into alkyl isocyanate and primary aromatic amine. The reaction of the former with primary alkyl amine borne by the oligosiloxane leads to alkyl-alkyl ureas that have been identified with the help of NMR. In terms of macromolecular structure, the formation of one alkyl-alkyl urea group implies that two polysiloxane segments are now consecutive in the copolymer chain. Thus, the formation of alkyl-alkyl ureas leads to an increase in the (average) number of successive polysiloxane segments that can reach value of 3-5. The longer PDMS blocks segregate in the shape of larger domains (~100 nm or more) depending on the composition of the material.

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Scheme captions

Scheme 1. Expected chemical reactions during the blending of E685 polyurethane with α,ω -aminopropyl PDMS oligomers: splitting of the urethane bond and subsequent reaction of isocyanate with amino-terminated oligosiloxane

Scheme 2. Reactions of urethane function and amino group of the silicone depicting aryl-alkyl, alkyl-alkyl and aryl-aryl ureas

Scheme 3. Scheme of the proposed structure of the TPU/PDMS chains (a) after the aryl-alkyl urea formation (b) when more and more aryl-alkyl ureas are replaced by alkyl-alkyl ureas formed later in the blending process

Scheme 4. Proposed chemical reactions during the high temperature blending of thermoplastic polyurethane (Elastollan 685A) with the thermoplastic polydimethylsiloxane-urea copolymer (Geniomer 80)

Figure Captions

Figure 1. Structure of the used polymers. a) Thermoplastic polyurethane elastomer E685, b) α,ω -aminopropyl oligosiloxane, c) Thermoplastic silicone elastomer Geniomer 80

Figure 2. Typical graph of evolution of the force exerted on the screws of the extruder (a) and changes in transparency of the blend E685/PDMS40D 90/10wt% prepared in the mini extruder with various residence times (A=2 min, B=12 min, C=22 min, D=27 min) (Note that the abrupt decreases of the force are just recorded when taking off a specimen)

Photos and corresponding transmission electron micrographs of the reactive blend E685/PDMS40D 90/10 wt%

A) after 3 minutes mixing. The reacted silicone appears in dark grey. The unreacted oligomer extracted from the material appears as white empty spots

B) after 12 minutes mixing, the first reaction is almost complete

C) after 22 minutes mixing, the morphology coarsens, leading to larger dark silicone domains

D) after 27 minutes mixing, the morphology continues to coarsen

Figure 3. SEM micrograph of a E685/PDMS40D blend (90/10 wt%) prepared at ambient temperature from THF solution. The silicone domains appear as nearly spherical holes while the TPU is matrix.

Figure 4. ^1H NMR spectrum of E685/PDMS40D blend 90/10 wt% after 12 minutes mixing time (THF- d_8 , 25°C). (a) CH_2OH from hydroxyl-terminated TPU, (b) $\text{CH}_2\text{NH}(\text{C}=\text{O})$ from aryl-alkyl urea, (c) $\text{CH}_2\text{NH}(\text{C}=\text{O})$ from alkyl-alkyl urea

Figure 5. ^1H NMR spectrum of E685/PDMS15D 90/10 wt% after 25 minutes of mixing (THF- d_8 , 25°C). (e1) $\text{CH}_2\text{NH}(\text{C}=\text{O})$ from alkyl-alkyl urea functions, (e2) $\text{CH}_2\text{NH}(\text{C}=\text{O})$ from aryl-alkyl urea functions, (f) aromatic protons of aryl-aryl urea groups, (g) aromatic protons of aryl alkyl urea groups, (h) NH of allophanate functions

Figure 6. E685/PDMS15D 90/10 wt% blend processed at 200°C. Evolution of primary amine groups of the oligosiloxane(◆), aryl-alkyl ureas (■) and alkyl-alkyl(▲) ureas of the TPU-co-PDMS copolymer as a function of mixing time (determined by NMR spectroscopy)

Figure 7. Transmission Electron micrograph of a) extruded blend of E685/Geniomer80 90/10 w%. Silicone appears as dark grey domains. b) E685/PDMS130D 90/10 wt% after 24 minutes blending at 200°C

Figure 8. Comparison between the final mass average molar masses obtained after the extrusion of the TPU with the amino-terminated oligosiloxane, PDMS40D (▲), or the thermoplastic silicone elastomer, G80 (■). The molar mass was normalized according to the molar mass of the neat, extruded TPU

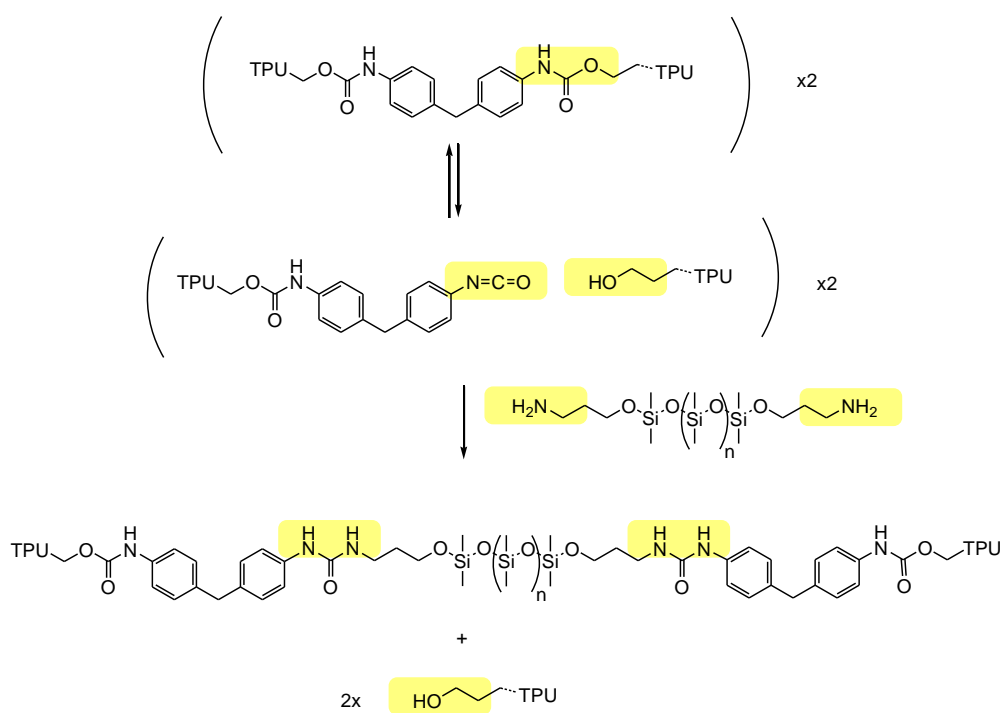
Table 1. Number average molar mass of the polymers determined by SEC in tetrahydrofuran.

| | Elastollan 685A | PDMS15D | PDMS40D | PDMS130D | Geniomer 80 |
|------------------------------------|-----------------|---------|---------|----------|-------------|
| \bar{M}_n (g.mol ⁻¹) | 136000 | 1240 | 3040 | 8520 | 176000 |

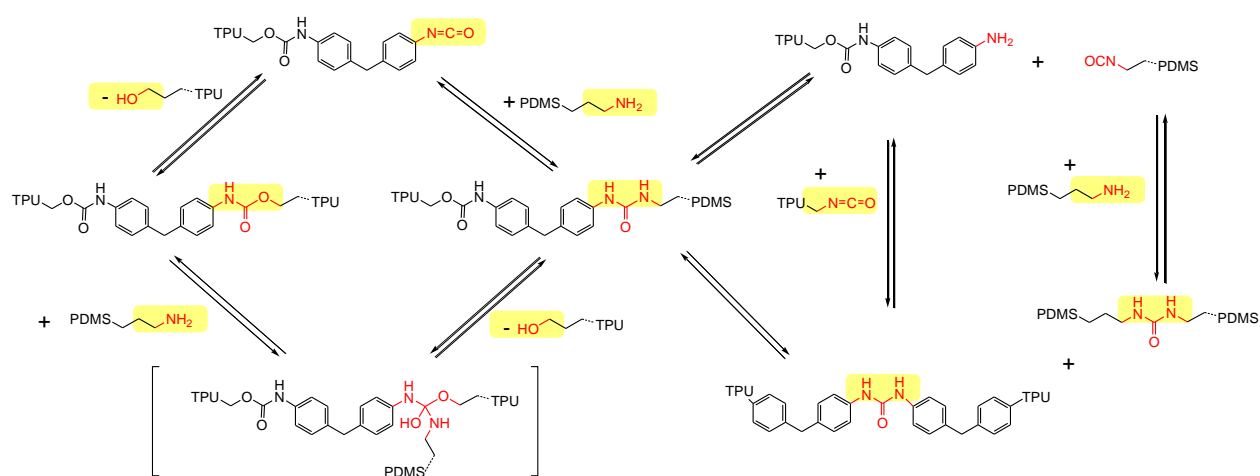
Table 2. Chemical groups ratio in E685/PDMS blends after different mixing times (^1H NMR determination).

| | Mixing time (min) | CH_2NH_2 of residual amine (mol%) | $\text{CH}_2\text{NH}(\text{C}=\text{O})$ of aryl-alkyl urea (mol%) | $\text{CH}_2\text{NH}(\text{C}=\text{O})$ of alkyl-alkyl urea (mol%) | Total (mol%) | Estimated number of adjacent polysiloxane segments, N | |
|---------|-------------------|---|---|--|--------------|---|-----|
| | | 2.60 ppm | 3.15 ppm | 3.06 ppm | | | |
| PDMS40D | 10 wt% | 12 | 0 | 64 | 28 | 92 | 1.9 |
| | | 22 | 0 | 37 | 43 | 80 | 3.3 |
| | | 27 | 0 | 33 | 60 | 93 | 4.6 |
| | 20 wt% | 27 | 0 | 47 | 35 | 82 | 2.5 |
| | | 37 | | 37 | 56 | 93 | 4.0 |
| | | 42 | 0 | 30 | 51 | 81 | 4.4 |
| | 30 wt% | 21 | 33 | 36 | 17 | 86 | - |
| | | 36 | 0 | 43 | 59 | 102 | 3.7 |
| | PDMS15D | 10 wt% | 10 | 16 | 70 | 20 | 106 |
| 15 | | | 0 | 68 | 31 | 99 | 1.9 |
| 18 | | | 0 | 60 | 37 | 97 | 2.2 |
| 25 | | | 0 | 54 | 53 | 107 | 3.0 |

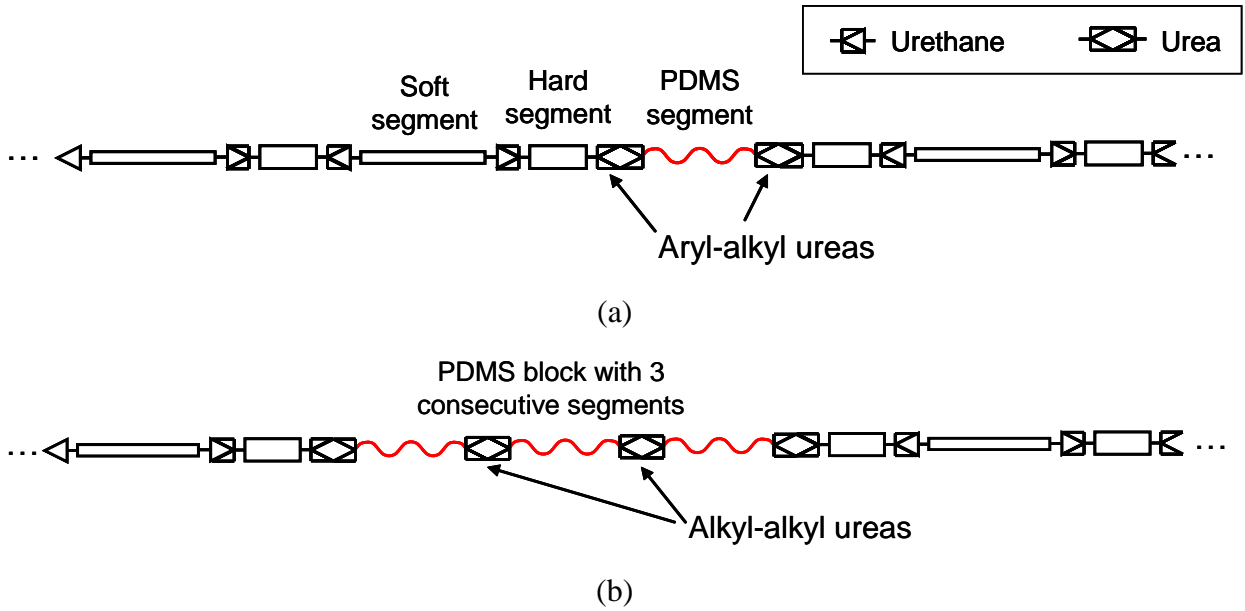
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Scheme 3. Scheme of the proposed structure of the TPU/PDMS chains (a) after the aryl-alkyl urea formation (b) when more and more aryl-alkyl ureas are replaced by alkyl-alkyl ureas formed later in the blending process



Scheme 4. Proposed chemical reactions during the high temperature blending of thermoplastic polyurethane (Elastollan 685A) with the thermoplastic polydimethylsiloxane-urea copolymer (Geniomer 80)

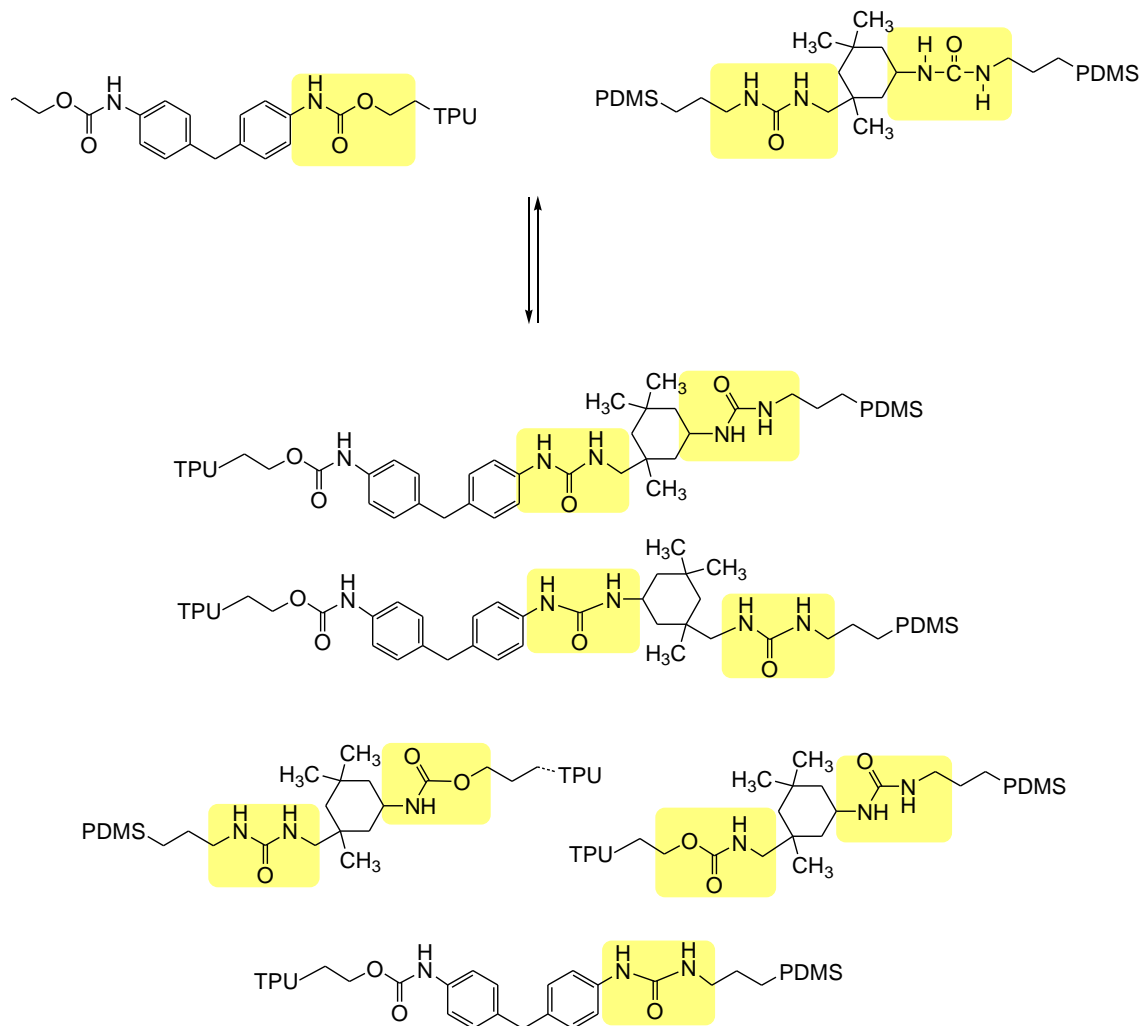


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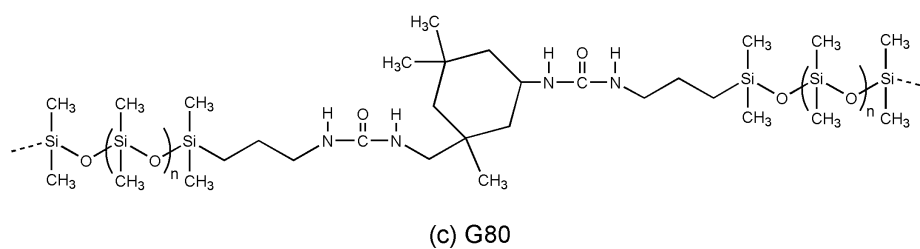
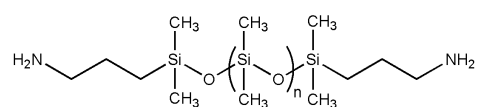
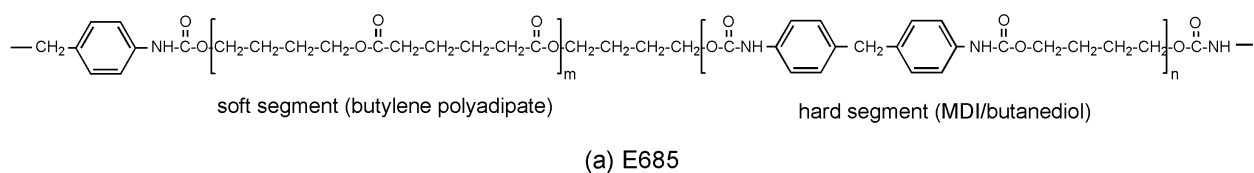


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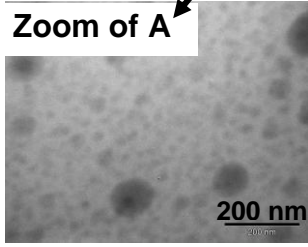
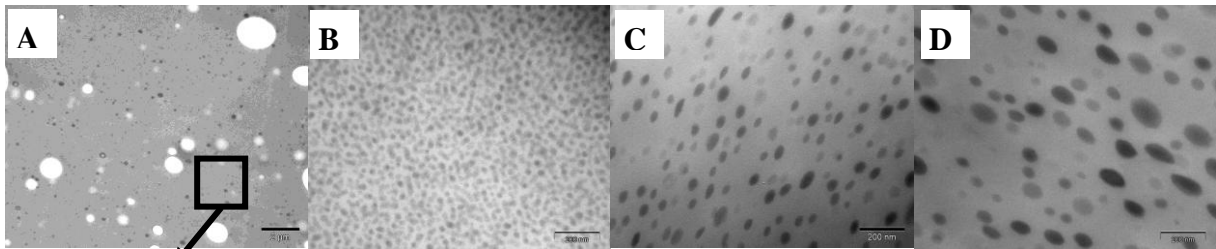
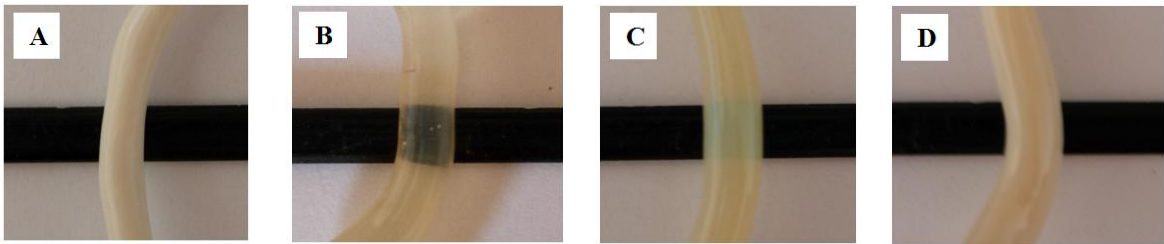
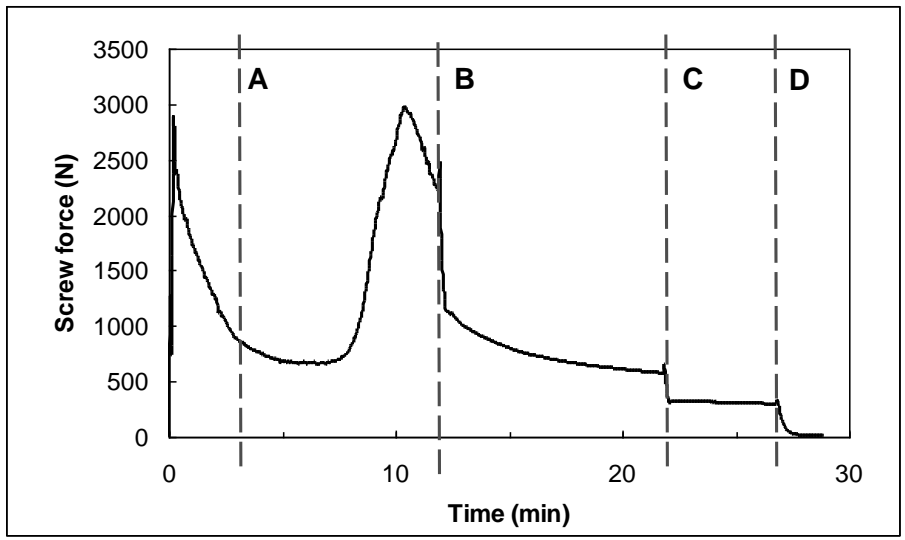
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a)



Scale bar for micrograph A = 2 μ m
Scale bar for micrographs B, C and D = 200 nm

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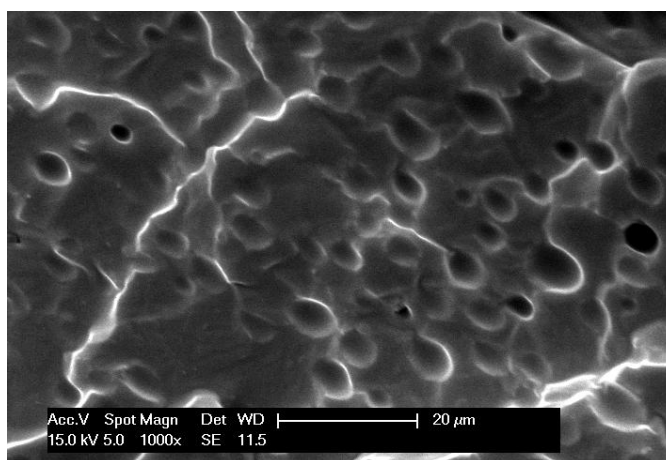


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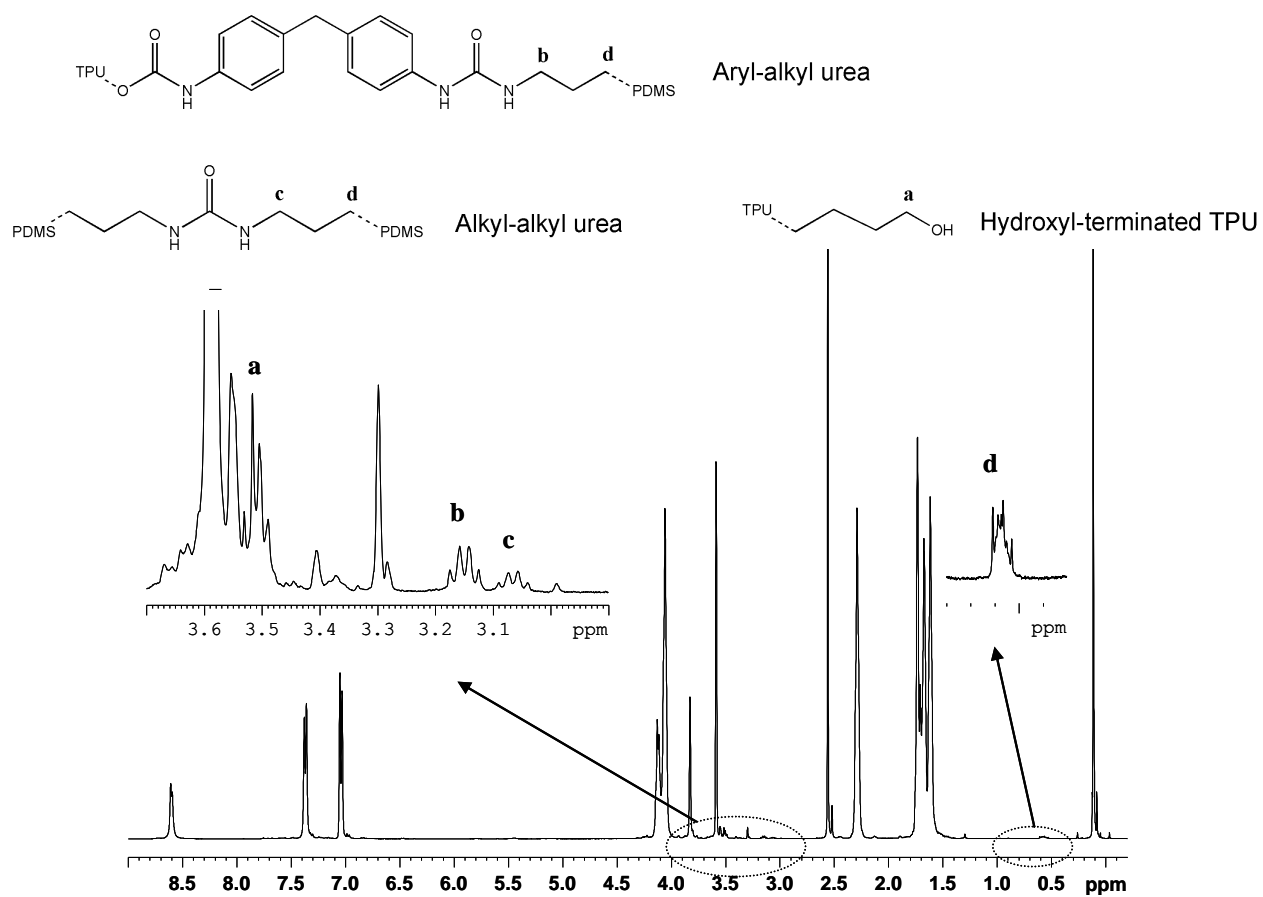


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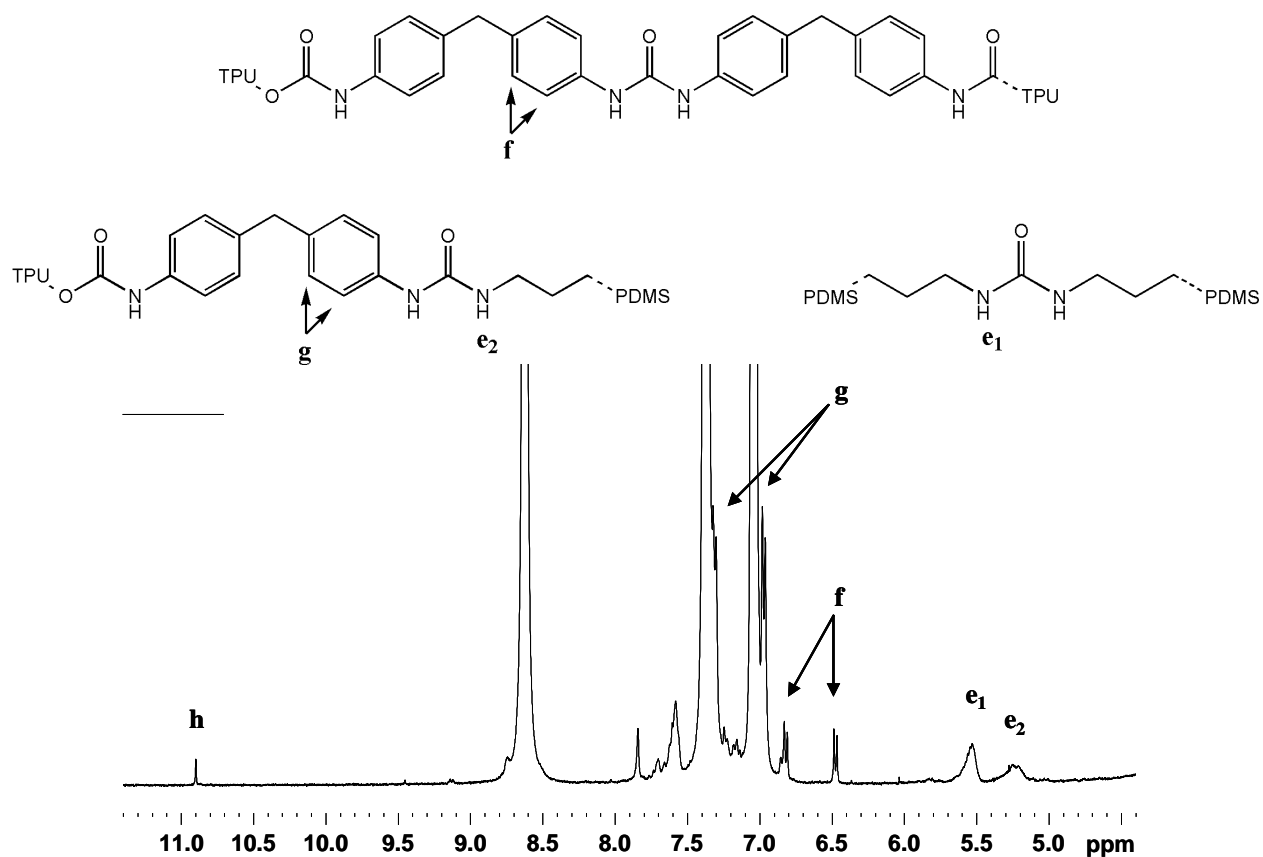


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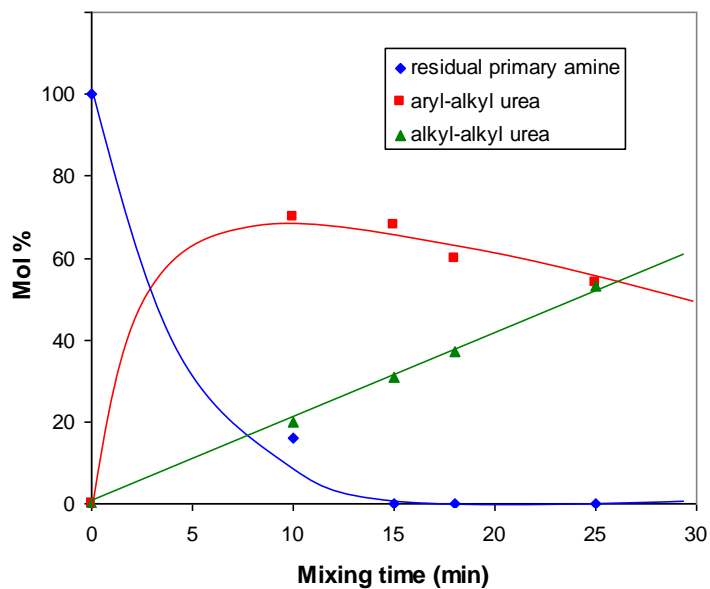
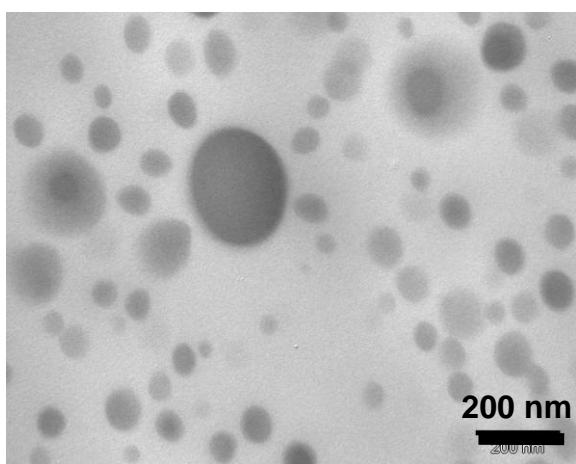
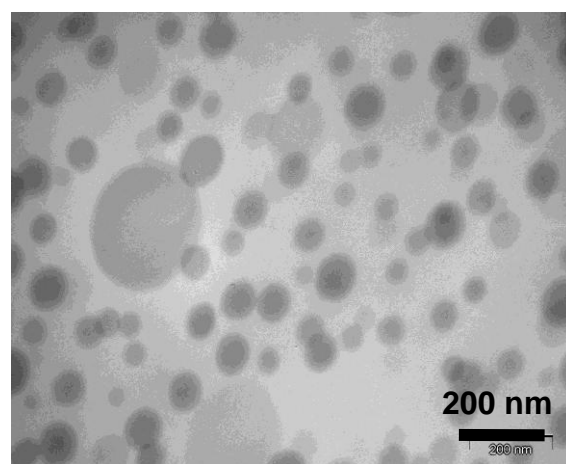


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(a)



(b)

Figure 8. Comparison between the final mass average molar masses obtained after the extrusion of the TPU with the amino-terminated oligosiloxane, PDMS40D (\blacktriangle), or the thermoplastic silicone elastomer, G80 (\blacksquare). The molar mass was normalized according to the molar mass of the neat, extruded TPU

