# SYNTHESIS AND CHARACTERIZATION OF SEGMENTED POLYURETHANES BASED ON POLYETHYLENE AND POLYTETRAMETHYLENE GLYCOLS

## PART 2: THERMO-MECHANICAL AND SWELING PROPERTIES

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## 1. Introduction

In the previous paper [1] we presented our study on the synthesis and characterization of some SPUs based on polyethylene and polytetramethylene glycols. Segmented polyurethanes (SPUs) are multiblock copolymers. Due to their specific phase separation characteristics caused by incompatibility between the hard and soft segments, they have quite good biocompatibility [2].

In this paper we present the second part of our study on the thermo-mechanical and swelling properties of the SPUs based on polyethylene and polytetramethylene glycols. The effects of the macrodiols on the properties of the SPUs obtained were discussed.

## 2. Experimental

### *2.1. Materials*

Polyethylene and polyteramethylene glycols selected for preparation of the polyurethanes are listed in the table 1. Before use they were carefully dried by azeotropic distillation of the toluene solution and subsequent removal of the solvent.

**Table 1**: Polydiols for preparation of SPUs

| Polyol | Mn $^{(a)}$ | Mn $^{(b)}$ | Tm, °C | Tg, °C |
|---|---|---|---|---|
| PEG-1000 | 1207 | 1100 | 40 | -70 (very weak) |
| PEG-2000 | 2341 | 2070 | 55 | -70 (very weak) |
| PEG-4000 | 4280 | 4109 | 62 | - |
| PTMO-2000 | 2186 | 1950 | 25 | -30 |

(a): Determined via GPC; (b): Determined via chemical titration

The hydroxyl number of the polyetherdiols for calculation of the molecular weights was determined by esterification of the polyetherdiols with acetic anhydride and subsequent titrimetric analysis of the carboxylic acid groups according to the standard procedure [3].

The molecular weights of the polydiols were also verified by means of gel permeation chromatography (PL columns, 103A°, 7mm i. d., 60 cm length, Polymer Laboratories Ltd, Shropshire, UK. Eluent: chloroform, Differential reflectometric detection (Model Waters 401, Millipore, MA, USA). Data analysis occurred on a waters data module model M730. Calibration was based on a peak position calibration curve established using polystyrene standards (Millipore, Millford, MA, USA).

Diisocyanate (MDCI) (Aldrich Bornem, Belgium) was vacuum distilled and stored under dried conditions in a refrigerator prior to use.

1,4-butane diol (Aldrich, Bornem, Belgium) was dried over calcium hydride for 2 days, distilled and stored under nitrogen.

Dibutyl tin diacetate was obtained from Aldrich (Bornem, Belgium) and used without further purification.

Dimethyl formamide (DMF) (Aldrich Bornem, Belgium) was dried over calcium hydride for 2 days and then vacuum distilled.

### *2.2. Characterization methods*

DSC thermograms were recorded on a Perkin-Elmer DSC under nitrogen purging (heating rate 10°C.min$^{-1}$, from -100°C to 100°C). The unit was equipped with a data processing module that allows substraction of the background and normalization for sample weight.

Uniaxial stress-strain experiments were carried out on a Hounsfield Test Equipment H10-KM at 25° C (film samples 20mm in length, 5mm wide, thickness: 0.12 - 0.15 mm, crosshead: 5mm.min$^{-1}$). The swelling test was carried out in distilled water and phosphate buffer solution (pH = 7.4) at different temperatures.

### *2.3. Polymer preparation*

The SPUs preparation was made according to the procedure described in the previous paper [1]. Briefly, the reaction for making the SPUs was carried out by two-stage procedure. In the first stage, the macrodiol (MD) in DMF reacts with diisocyanate (DI) with the molar ratio MD/DI : 1/2, at 90°C for 2 hours. Dibutyl tin diacetate was used as catalyst. The reaction mixture was then cooled down to the room temperature. Afterward 1,4-butane diol as a chain extender was added and the chain extension reaction was carried out at 90°C for 2 hours. The end copolymer product was precipitated in water. After drying it was redissolved in THF and reprecipitated in the solvent mixture hexane-ether (1/1). The copolymer product was dried under vacuum at 60°C at least for 2 days.

## 3. Results and discussion

### 3.1. NMR spectra and IR analysis

The structure of the SPUs obtained was confirmed by proton NMR and IR spectra. The NMR and IR absorption bands of the SPUs were shown in the previous paper [1].

### 3.2. DSC analysis of SPUs

The soft segment glass transition temperature (Tg) and the melting temperature (Tm) of the SPUs obtained from the DSC data are summarized in the *table 2*.

**Table 2:** DSC data of SPUs

| Code | Polyol ratio | Tg, °C | Tm, °C |
|---|---|---|---|
| PU-1 | PEG-1000 + PTMO-2000 (1/1) | - | -121.5 |
| PU-2 | PEG-2000 + PTMO-2000 (1/1) | -55 | 35.5 / 20 |
| PU-3 | PEG-4000 + PTMO-2000 (1/1) | -60 | 48 / 18 |
| PU-4 | PEG-2000 + PTMO-2000 (1/2) | -60 | 34/18 |
| PU-2 | PEG-2000 + PTMO-2000 (1/1) | -55 | 35.5 / 20 |
| PU-5 | PEG-2000 + PTMO-2000 (2/1) | -60 | 40 / 27 |

The polymers show the melting temperature (Tm) which increases with increasing the molecular weight of the polyethylene glycols. Possibly, this is due to an increase in the size of the soft segment crystallinity. The increasing of the crystalline domain probably restricts the solubilization of the hard segments into the soft segments and consequently makes the system more incompatible. This implies that the material becomes more phase separated. Following from PU-4 to PU-2 and to PU-5 we can see that the Tm increases with increasing the PEG-2000/PTMO-2000 ratio. The increase in ratio between PEG-2000 and PTMO-2000 means the increase in crystalline domain. This causes again the enhancement of the phase separation. This result is in agreement with that of other authors [2,4,5].

### 3.3. Tensile properties

The tensile properties of the SPUs are shown in the table 3.

**Table 3:** Tensile properties of the SPUs

| Code | Polydiol ratio | Tensile at break, MPa | Ultimate Tensile, MPa | Elongation at break, % |
|---|---|---|---|---|
| PU-1 | PEG-1000 + PTMO-2000 (1/1) | 7.0 | 8.5 | 650.0 |
| PU-2 | PEG-2000 + PTMO-2000 (1/1) | 12.1 | 12.6 | 570.2 |
| PU-3 | PEG-4000 + PTMO-2000 (1/1) | 15.2 | 15.7 | 480.0 |
| PU-4 | PEG-2000 + PTMO-2000 (1/2) | 9.0 | 10.6 | 600.4 |
| PU-2 | PEG-2000 + PTMO-2000 (1/1) | 12.1 | 12.3 | 555.2 |
| PU-5 | PEG-2000 + PTMO-2000 (2/1) | 13.8 | 14.0 | 490.0 |

When comparing PU-1 with PU-2 and PU-3 we can see the increase in tensile strength upon increasing the molecular weights of the polyethylene glycols. DSC data have shown that the phase separation was increasing from PU-1 to PU-3. On the other hand, the crystalline domain of the soft segments in the SPUs is increasing from PU-1 to PU-3 too. Thus, larger crystalline domain in the soft segments could be the cause for the better tensile properties of the resulted SPUs. The same law can be observed when comparing PU-4 with PU-2 and PU-5. An increase in ratio of PEG-2000 to PTMO-2000 means the increase in crystalline domain of the soft segments and would be the reason for improving the tensile strength of the SPUs.

### *3.4. Swelling study*

The swelling study was carried out in distilled water at different tempertures, the results are shown in figure 1:

For the all SPUs samples, the swelling decreases with rising temperatures. When comparing PU-1 with PU-2 we see the swelling of PU-2 is much higher than that of PU-1. This is due to lareger crystalline domain of the soft segments in PU-2 compared to that in PU-1.

If we compare PU-4 with PU-2 and PU-5, we can see also the increase in swelling from PU-4 to PU-2 and to PU-5. Here again, the reason would be the same: the increase in swelling is due to enhancement of the crystallinities from PU-4 to PU-2 and to PU-5.

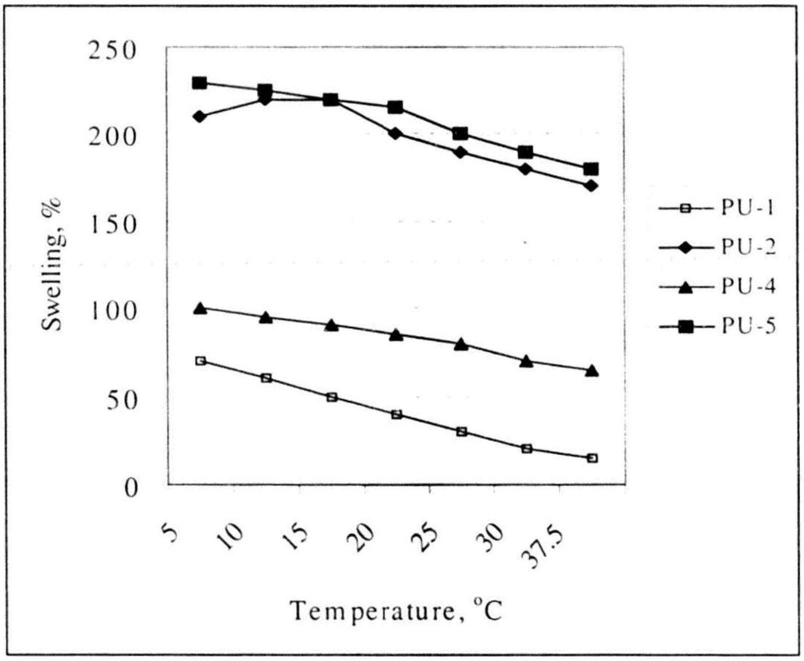
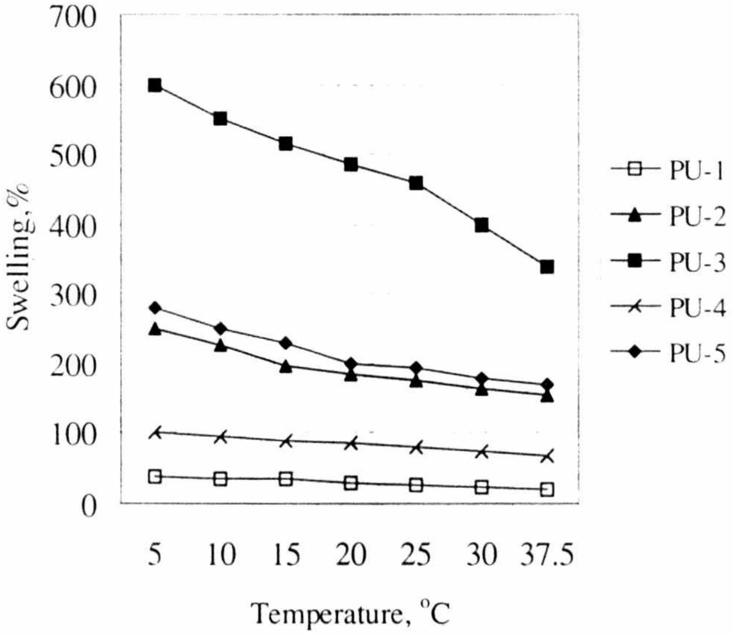


**Figure 1:** The swelling curves of the SPUs in water at different temperatures

The same swelling behaviour of the SPUs in buffer solution can be observed in Figure 2.

Comparing PU1 with PU2 and PU3 we can see that when molecaular weight of the soft segments of SPUs is increasing from PU1 to PU2 and PU3, the swelling is also increasing from PU1 to PU2 and PU3. The swelling is increasing from PU4 to PU2 and PU5 when the ratio PEO-2000: PTMO 2000 in the soft segments is increasing. It can be therefore concluded that the swelling behavior of the selected SPUs for study is strongly dependent on the PEO amount and PEO molecular weight.



## 4. Conclusion

The data obtained show that the increase in PEO amount as well in PEO molecular weight of the macroether diols in the SPUs soft segments results in enhancement of their crystalline domain making the SPUs more phase separated. The mechanical and swelling properties of the SPUs are increasing upon increasing the crystalline domain of the soft segments in the SPUs as well.

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# TỔNG HỢP VÀ KHẢO SÁT TÍNH CHẤT CỦA CÁC POLYURETAN PHÂN ĐOẠN (PU) TRÊN CƠ SỞ POLYETYLEN GLYCOL VÀ POLYTETRAMETYLEN GLYCOL

## (PHẦN II: NGHIÊN CỨU TÍNH CHẤT CƠ LÝ VÀ ĐỘ TRƯƠNG)

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Trong bài báo trước (1) đã nghiên cứu phương pháp tổng hợp, đặc trưng cấu trúc và hình thái học của một số polyuretan (PU) trên cơ sở polyetylen glycol và polytetrametylen glycol. Bài báo này đề cập về nghiên cứu tính chất cơ lý và độ trương của các loại PU trên trong nước và dung dịch đệm. Đã thảo luận về ảnh hưởng của thành phần và cấu trúc của monome ban đầu lên tính chất cơ lý và độ trương của PU sản phẩm.

*Từ khóa: Polyuretan phân đoạn, tách pha, tính chất cơ lý, độ trương.*