

# STUDY ON SEGMENTED POLYURETHANE WITH MIXED SOFT SEGMENTS OF POLYCHLOROMETHYL METHYL SILOXANE AND POLYTETRAMETHYLENE OXIDE \*

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## ABSTRACT

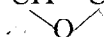
Two series of polyurethanes based on mixed polychloromethyl methyl siloxane and polytetramethylene oxide in different weight fractions were synthesized. The phase separation of samples was studied using DSC and dynamic mechanical property analysis. The results showed that the introduction of chloromethyl group into polysiloxane increased its polarity and hence improved the miscibilities with polytetramethylene oxide and polyurethane hard segment. Particularly, in the case of N-methyldiethanolamine extended materials, the surface and tensile properties of these samples can be adjusted by various ratios of two soft segments.

## INTRODUCTION

Thermoplastic polyurethane elastomers are (A-B) $_n$  type block copolymers, consisting of alternating flexible and rigid chain segments. In the case of the conventional segmented linear polyurethanes the soft segments are low molecular weight (600—3000) polyether, polyester or polyalkene macroglycols, the hard segments are consisting of diisocyanate and a low molecular weight diol extender. The polarity difference between two segments and the ability of the urethane segments to form interurethane hydrogen bonds are the main driving forces which cause these materials to have micro-phase separation morphology<sup>[1-3]</sup>. Recently, polyurethanes based on polysiloxane soft segments have been investigated<sup>[4]</sup>, these materials are very attractive because the polysiloxane soft segments may improve certain bulk and surface properties of the polyurethane block copolymers, such as a broad service temperature due to the very low  $T_g$  of polydimethylsiloxane ( $-123^\circ\text{C}$ ), good oxidation resistance and electrical properties. Particularly the polysiloxane segments which have very low

surface energies, tend to migrate to the air-polymer interface and may provide the material a very hydrophobic and physiologically inactive surface. Thus siloxane-containing polyurethane may have a wide range of potential applications such as elastomer, coating, biomaterial and environmental stable material.

McGrath and coworkers<sup>[4-6]</sup> have recently reported the synthesis of siloxane oligomers with various well-defined difunctional terminal groups, such as  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{CH}=\text{CH}-$ ,  $>\text{NH}$  and the reaction kinetic



study of non-chain extended polysiloxane urethane. Yu and Cooper et al.<sup>[7]</sup> have reported the synthesis, morphology and properties of hydroxybutyl terminated polydimethylsiloxane polyurethane and related ionomers. All of their data showed that the mechanical properties of polydimethyl siloxane polyurethane are much inferior to these of polyether or polyester polyurethanes. For example, the tensile strength of polydimethylsiloxane polyurethane are only 3–10 MPa with elongation at break of 200–600%, while the typical commercial polyether or polyester polyurethanes possess tensile strength of 30–60 MPa with elongation at break of 300–1000%. Efforts have been made to comprise the hydrophobic surface and strong tensile properties of polyurethane elastomers, but only a limited progress achieved so far<sup>[8,9]</sup>.

In this investigation we intend to develop a new polysiloxane polyurethane material which has both good mechanical properties of polyurethane and hydrophobic surface of polysiloxane. For this purpose a series of segmented polyurethanes based on the mixtures of  $\alpha, \omega$ -dihydroxybutyl terminated polychloromethyl methyl siloxane (HTPCS) and  $\alpha, \omega$ -dihydroxypolytetramethylene oxide (PTMO), 4, 4-diphenylmethane diisocyanate (MDI) and extender either butanediol (BD) or N-methyldiethanolamine (MDEA) were synthesized.

## EXPERIMENTAL

### *Material synthesis*

4, 4-diphenyl methane diisocyanate (MDI), chloromethyl methylchlorosilane, 1, 4-butanediol (BD) and N-methyldiethanolamine were purified by vacuum distillation. Anhydrous N,N-dimethyl acetamide (DMA) and  $\alpha, \omega$ -dihydroxypolytetramethylene oxide (PTMO) of molecular weight 1000 were further dehydrated under vacuum at room temperature for

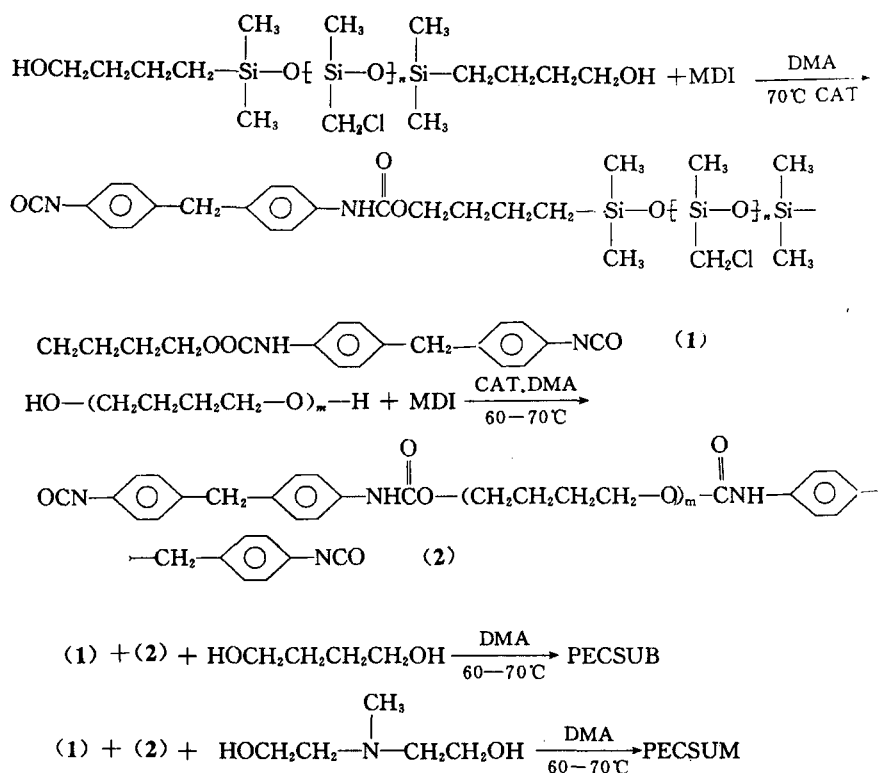
48 hours. Stannous octoate catalyst and 1, 3-bis (4-hydroxybutyl) tetramethyldisiloxane ( HT ) were used as received. 60g chloromethyldichlorosilane, 5.4 g 1, 3-bishydroxybutyldimethylsiloxane, 100g water and a small amount of concentrated hydrochloric acid were added into a flask. The reaction mixture was stirred for 16 hours at room temperature. The hydrolytic product was extracted by ether, the ether solution was washed with a 5%  $\text{NaHCO}_3$  solution repeatedly to neutralize the excess acid, then dried over anhydrous  $\text{MgSO}_4$ . A colorless viscous liquid (HTPCS) was obtained after evaporation of the ether and volatile cyclic siloxane.

The molecular weight of HTPCS oligomer was determined to be 2014 and 2085 by using  $^1\text{H-NMR}$  and vapor pressure osmometry respectively. The segmented polyurethanes with mixed soft segment of polychloromethyl methyl siloxane and polytetramethylene oxide were synthesized in N, N-dimethylacetamide solution by the three-step condensation reaction as shown in scheme 1. First, under the protection of dry nitrogen, the HTPCS solution contained 0.15% stannous octoate as catalyst, was added to the stirred MDI solution slowly at 50—60 °C, then the solution of PTMO was added and continued stirring at 60—70 °C for an hour, BD or MDEA was added and stirred at the same temperature range for 2 hours. The polymer was precipitated into hot distilled water, washed with ethyl alcohol for several times and then dried in a vacuum oven at 70—80°C for at least 2 days.

Table 1 showed the compositions of the polyurethane samples. The polymer PECSUM-15 represents an MDEA chain extended sample in which the weight fraction of polychloromethyl methyl siloxane in total soft segments is 15%, the molar ratio (PTMO + HTPCS) : MDI : BD (or MDEA) of all samples is 1 : 2 : 1.

**Table 1** The compositions of the polyurethane samples

|           | HTPCS(mol) | PTMO(mol) | MDI(mol) | BD(mol) | MDEA(mol) |
|-----------|------------|-----------|----------|---------|-----------|
| PECSUB-0  |            | 0.01      | 0.02     | 0.01    |           |
| PECSUM-0  |            | 0.01      | 0.02     |         | 0.01      |
| PECSUB-15 | 0.0008     | 0.00982   | 0.02     | 0.01    |           |
| PECSUB-25 | 0.00142    | 0.00872   | 0.02     | 0.01    |           |
| PECSUM-15 | 0.0008     | 0.00982   | 0.02     |         | 0.01      |
| PECSUM-25 | 0.00142    | 0.00872   | 0.02     |         | 0.01      |



Scheme 1

Test methods:

Film of block polymer were cast from 10% DMA solution, dried in a vacuum oven at 65—75°C for 3 days, and then stored in a desiccator at room temperature.

Contact angle data were obtained using a RAME—HART model 10000 apparatus.

Differential scanning calorimetry (DSC) thermograms over the temperature range —150 °C to 200 (or 250) °C were recorded using a Perkin-Elmer DSC 2C or Rigaku 8150. The heating rate is 20 °C/min under a He purge.

Dynamic mechanical data were obtained using a computer controlled Rheovibron DDV-II. Data were taken from  $-150^{\circ}\text{C}$  until the sample failed at a test frequency of 110 Hz, the heating rate was  $2^{\circ}\text{C}/\text{min}$ .

Room temperature uniaxial stress-strain data were taken on an Instron Model TM instrument, samples were prepared using an ASTM D 1708 standard die.

## RESULTS AND DISCUSSION

### *Synthesis*

It is well known that polysiloxane has a very low solubility parameter, the urethane hard segments obtained by the reaction of MDI and chain extender are highly polar and have much higher solubility parameters ( $>10$ ). The large polarity difference of reactants makes trouble to find a common solvent.

McGrath<sup>[6]</sup>, has utilized mixed solvent, for example DMA + THF or DMA + EEE (2-ethoxyethyl ether) during the chain extension, but the molecular weight of the extended polymers was always in the low range.

In this investigation, as we expected, replacing 50% of methyl group of polydimethylsiloxane with chloromethyl group dramatically improved the solubility of the siloxane oligomer in polar solvents. Dimethylacetamide could be used satisfactorily as a common solvent to prepare polysiloxane-polyurethane based on polysiloxane-polyether mixed soft segments.

### *Surface wetting test*

When a drop of liquid rest on surface, unless spreading takes place the liquid-vapour interface will form a finite angle with solid surface. This angle is termed the contact angle and usually given the symbol of  $\theta$ . If the liquid is water and the solid is a polymer, the values of contact angle will indicate that the polymer is either hydrophilic or hydrophobic, which are related to the blood compatibility.

In Table 2, some contact angle data of polyurethane based on polydimethylsiloxane and mixed polydimethylsiloxane-polytetramethylene oxide soft segments were listed. It was shown that instead of polydimethylsiloxane, incorporation of polychloromethyl methyl siloxane with polyether was still effective to build a rather hydrophobic surface for polyurethane.

**Table 2** Contact angle of water on the samples

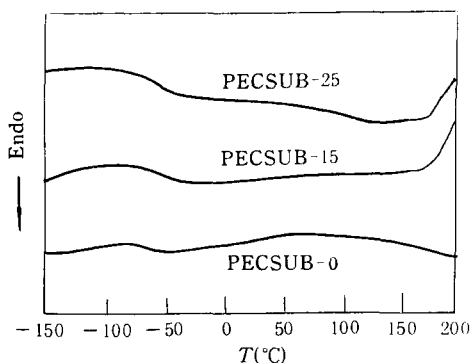
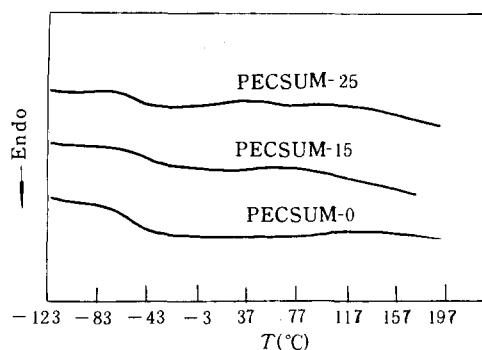
| Sample    | Contact angle(rad) | Sample    | Contact angle(rad) |
|-----------|--------------------|-----------|--------------------|
| PECSUB-0  | 1.31               | PECSUM-25 | 1.53               |
| PECSUB-15 | 1.36               | PESUM-15  | 1.66               |
| PECSUB-25 | 1.55               | PESUM-25  | 1.69               |
| PECSUM-0  | 1.31               | PDMS      | 1.83               |
| PECSUM-15 | 1.36               |           |                    |

\* PESUM is polydimethylsiloxane-polyether polyurethane

\*\* PDMS is polydimethylsiloxane

### Thermal analysis

DSC thermograms for the PECSUB and PECSUM samples are shown in Figs. 1 and 2. The glass transition temperature data are summarized in Table 3. From these data, it can be found that the glass transition temperature of polychloromethyl methyl siloxane is about 30°C higher than polydimethylsiloxane, and for various proportions of PTMO/HTPCS in BD-extended samples (PECSUB-0, PECSUB-15 and PECSUB-25) the  $T_g$  of soft segment is not affected by the increase of the HTPCS weight fraction.

**Fig. 1** DSC curves of PECSUB**Fig. 2** DSC curves of PECSUM**Table 3** Glass transition temperature of soft segments

| Sample   | PTMO      | HTPS     | HTPCS     | PECSUB-0  | PECSUB-15 |
|----------|-----------|----------|-----------|-----------|-----------|
| $T_g$ °C | -82       | -120     | -87       | -53       | -55       |
| Sample   | PECSUB-25 | PECSUM-0 | PECSUB-15 | PECSUM-25 |           |
| $T_g$ °C | -55.5     | -54      | -43       | -47       |           |

However, in the case of MDEA-extended polymers, the  $T_g$  of soft segment increased considerably with the increase of HTPCS weight fraction. The  $T_g$  of PECSUM-15 is 11°C higher than the  $T_g$  of the sample

PECSUM-0. These results indicated that the introduction of chloromethyl group in polysiloxane increased the polarity and solubility parameter and hence improved the compatibility of PTMO soft segment phase and hard segment phase. As we expected, for MDEA-extended polymers the chloromethyl group in soft segment does interact with tertiary amine of MDEA. This interaction caused an amount of hard segment to dissolve in soft segments, then the degree of phase mixing increased.

As to that why the  $T_g$  of PECSUM-25 is lower than the  $T_g$  of PECSUM-15, it can be explained by the excess of chloromethyl groups over the content required for interaction with tertiary amine in hard segments. According to the calculation of 1 : 1 molar ratio of chloromethyl and tertiary amine in PECSUM system, 12 wt% of HTPCS in total soft segments is stoichiometric amount for interaction with tertiary amine of MDEA. Excess of HTPCS does not benefit to further phase mixing.

#### *Dynamic mechanical analysis*

Fig. 3 showed the dynamic mechanical properties of the same hard segment content materials with different proportion of HTPCS and PTMO. There are two loss peaks ( $E''$ ) at low temperature region, the one around  $-120^\circ\text{C}$  is related to the local model motion of PTMO, the other loss peak is the glass transition temperature of the soft segment phase.

Fig. 3 also showed  $E''$  peak position of PECSUM-15 is at higher temperature than PECSUM-25, this result coincided with DSC analysis. The storage modulus of PECSUM-15, PECSUM-25 and PECSUM-0 above the  $T_g$  of soft segment gradually increased (Fig. 3). This phenomenon supported the above elucidation, the interaction of chloromethyl in soft segment with tertiary amine in hard segment decreased hard domain cohesion, and hence decreased the storage modulus of plateau region.

#### *Stress-strain analysis*

Typical stress-strain curves for the mixed soft segment polyurethane

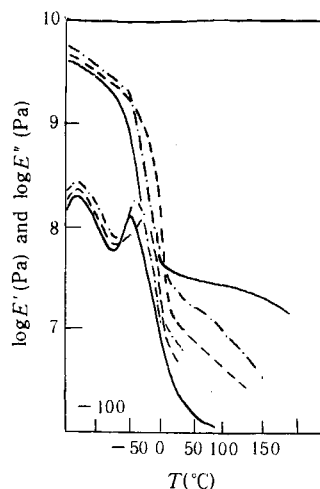


Fig. 3 The storage modulus ( $E'$ ) and loss modulus ( $E''$ ) for PECSUM  
— PECSUM-0; --- PECSUM-15;  
- · - PECSUM-25

were shown in Figs. 4 and 5. Table 4 summarized the tensile properties of

**Table 4** Tensile properties of samples

| Sample    | $\sigma_b$ (MPa) | $\epsilon_b$ (%) | E (MPa) |
|-----------|------------------|------------------|---------|
| PECSUB-0  | 39.2             | 650              | 46.6    |
| PECSUB-15 | 14.7             | 700              | 18.6    |
| PECSUB-25 | 7.06             | 800              | 14.7    |
| PECSUM-0  | 41.2             | 650              | 38.8    |
| PECSUM-15 | 12.1             | 800              | 5.6     |
| PECSUM-25 | 29.8             | 700              | 21.6    |

$\sigma_b$  = Ultimate stress

$\epsilon_b$  = Elongation at break

E = Young's modulus

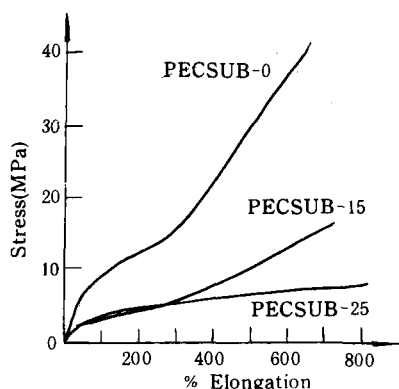


Fig. 4 The stress-strain curves for PECSUB

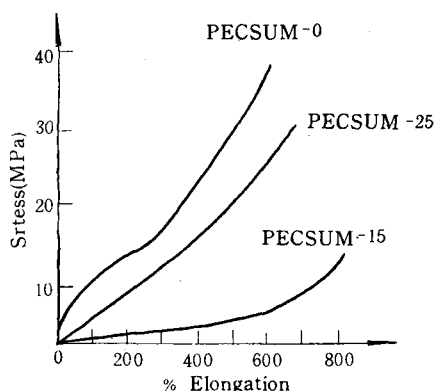


Fig. 5 The stress-strain curves for PECSUM

the samples. These data showed that in both PECSUB and PECSUM system the tensile strength largely dropped with the introduction of polychloromethylsiloxane. In the case of PECSUB samples the tensile strength is in the order of  $\text{PECSUB-0} > \text{PECSUB-15} > \text{PECSUB-25}$ , however PECSUM series followed the order of  $\text{PECSUM-0} > \text{PECSUM-25} > \text{PECSUM-15}$ . Thus two conclusions can be made:

First, incorporation of polychloromethylsiloxane with polytetramethylene oxide in soft segment was unfavorable to the tensile property particularly for the BD-extended sample. Secondly, as compared the MDEA-extended system with the BD-extended polyurethanes, the effects of polychloromethyl methyl siloxane on the phase separation and mechanical properties are different. In PECSUM-25 sample, a reasonable degree of phase separation made its tensile strength raise to 30 MPa with an ultimate elongation of 700%, which was already close to the commercial polyurethane without polysiloxanes. This result is attractive, which means a potential material whose surface hydrophobic property is similar to that of

polysiloxane and mechanical properties are close to those of polyether polyurethane could be obtained by adjusting the ratio of polychloromethyl methyl siloxane to polytetramethylene oxide and selecting a suitable weight fraction of hard segment and extender MDEA.

**Keywords:**

Mixed soft segments; Polychloromethyl methyl siloxane; Polyurethane; Micro-phase separation

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