REVIEW ON HARD SEGMENT INFLUENCESON THE PHYSICALPROPERTIES OF THERMOPLASTICPOLYURETHANES

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ABSTRACT.*Thermoplastic polyurethanes (TPUs) are the fastest growing market in polyurethane technology mainly due to their easy process ability, versatile properties and recyclable nature. They find applications in high performance materials like coatings, adhesives, fibres and foams in a variety of industries ranging from automotive and footwear to medical implants. TPUs are linear block copolymers comprising of alternating soft and hard segments. The versatile properties of TPUs are usually attributed to their phase-separated morphologies. Different parameters are known to affect TPUs physical properties. One of those is their chemical architecture that is the statistical arrangement of hard segments (HS) and soft segments (SS).In particular the architecture of the HS will influence the molecular structure and intermolecular interaction. Its role as physical crosslink sites will govern thermal, mechanical and morphological properties. Hence a modification of HS chemical architecture might adjust the ultimate properties of TPU. This implication is important in process control of production and design of application. Therefore this paper will review various studies to understand the effect of different architecture to the properties of TPU.*

Keywords: thermoplasticpolyurethanes, hard segment architecture, physical properties

INTRODUCTION

Polyurethanes are very versatile and diversely formulated material. They can be tailor-made with a remarkable accuracy to meet the needs of a particular application (Woods, 1990). Their properties range from soft to hard, high to low resilience and from cellular to solid (non-cellular). They can be manufactured as foam, solid, elastomers and fibres.

Thermoplastic polyurethane elastomersare segmented, linear multiblock copolymers. These non-cellular polyurethanes are mainly based on alternating blocks of rigid, hard segments (HS) and flexible, soft segments (SS) (see Figure 1). TPU is the first and still important thermoplastic elastomers. It was the first synthetic material with rubber elasticity that could be processed by thermoplastic methods (Oertel, 1985).

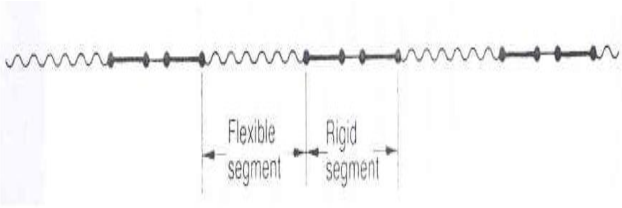

Figure 1. Primary structure of polyurethanes (Uhlig, 1999).

TPUs bridge the gap between thermoplastic and rubber, by having physical properties coverage in parts of and in between both materials. By varying the types and amounts of the raw materials, there are more combinations of properties possible than with almost any other material available. TPU also offers higher tensile strength, elongation and tear resistance compared to other thermoplastic elastomers (www.polyurethane.org, 2003).

TPU has excellent properties with a wide range of applications in the following industries: films and sheet, hose, shoes, automotive, medical and in engineering applications (Woods, 1990; Oertel, 1985; Legge et al.,1987).

The main properties required in those applications are as follows:
- high abrasion and puncture properties, high cut and tear propagation resistance
- high tensile strength, elasticity, elongation, flexural strength, and varying stiffness
- high impact strength especially at low temperature,
- good weathering resistance against: hydrolysis, microbes, oil, fuel, UV and ozone
- low air permeability, good weldability, and being lighter in weight than rubber
- good compatibility/compliance with human body, biodegradable and ability to form microporous structure.

TPU can be processed by conventional thermoplastic techniques like injection moulding, extrusion and calendering. During the processing, TPU granule or sheet must resist the following thermal and mechanical treatments (Oertel, 1985):
- high processing temperature 170 – 220 °C
- high operating pressure of machinery, up to 1,000 bar
- high torsional force in friction welding
- high temperature of hot air / nitrogen or mirror welding 270 – 330 °C
- high temperature of post curing 80 – 120 °C for 15 – 20 hours.

Those excellent physical properties of TPU derive from their microphase-separated structure. The TPU microstructure is influenced by at least two factors: chemical architecture (chemical composition, block length and molecular weight), and preparation technique (thermal and mechanical history).Researches in this area revealed the significant of these effects, but yet the influence is not fully understood.

This paper will discuss the chemistry and microstructure of TPU, followed by thermal, mechanical and morphological properties, which are specifically affected by the hard segments architecture.

TPU CHEMISTRY

TPU are non-cellular, solid polyurethanes (Uhlig, 1999) which are typically multiblock copolymers comprising of alternating “soft”, flexible, saturated aliphatic polyether polyols or polyester polyols segments (SS) and “hard”, rigid or stiff polyurethane segments (HS). The HS comprises difunctional isocyanates and low molecular weight diols or diamines chain extender.

The most widely used diisocyanates are mainly aromatic because they are economically more readily available with higher reactivity (Oertel, 1985). *Para* gives higher reactivity than *ortho* configuration (Woods, 1990). The aromatic isocyanatesare particularly important for the production of high quality TPU. However, where color and clarity retention during exposure to sunlight is a high priority, an aliphatic hard segment is typically recommended(www.polyurethane.org, 2003).

A low molar mass chain extender is used to improve the properties of the segments. The chain extender may be diol or diamine. Diamine gives the hardest elastomer with the highest Young’s modulus, because the hard block domains have the highest three-dimensional physical crosslinks density. This crosslinks will reduce the thermoplasticity, hence a faster curing that further reduce the production cycle. The three-dimensional hydrogen bonding is made possible by the extra amine group in the urea linkage(Macosko, 1989). This extender also gives higher polarity difference between HS and SS, compared to TPU extended by diol. This leads to improved phase separation, thus higher thermal stability and tensile modulus.

The polyol used may be polyether or polyester. About 90% of TPU is polyether-based, because polyether polyol is cheaper than polyester polyol. However, polyester polyol can give higher abrasion, tensile and tear properties, and a better weather resistance (particularly to oil).

Polyether polyol gives the following properties (Woods, 1990):

- highest resilience and good low temperature performance
- good resistance to hydrolysis and microbial organism attack
- more sensitive to heat and lower glass transition temperature (T_g)
- better mechanical properties due to less hydrogen bonding with HS(Macosko, 1989)

Polyether-based TPU has a larger degree of phase separation than the analogous polyester-based TPU, because it is less compatible with MDI (Woods, 1990 and Lamba et al., 1998). Hydrogen bonding between urethane and ketone group is less favourable than that of carbonyl group in polyester. In this case, HS domain tends to be larger and more complex.
An example of PU forming reaction and structure with diol chain extender is represented schematically as follows:

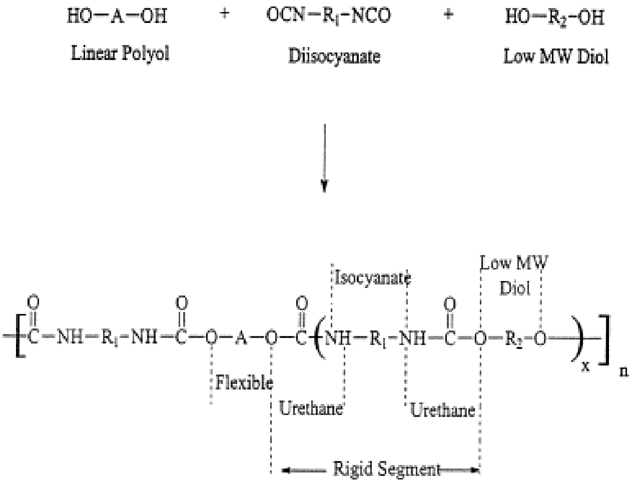

Figure 2. Polyurethane Formingand Structure (Crawford et al., 1998)

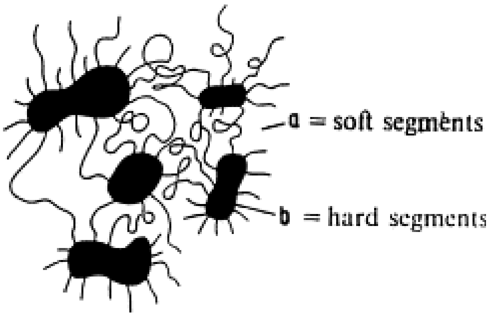

Figure3. Hard Segments and Soft Segments of ThermoplasticPolyurethanes (Oertel, 1985)

TPU MICROSTRUCTURE

Generally, the hard and soft segments of polyurethanes have a positive heat of mixing and are therefore incompatible (Lamba et al., 1998). Thermodynamic incompatibility of these segments, often combined with crystallisation of either or both segments below T_g (glass transition temperature), drives their microphase separation into hard and soft phases above T_g(Oertel, 1985). The two-phase polyurethane microstructure is resulting from the physical bonding and aggregation of the hard segments of adjacent polymer chain(Woods, 1990). This microphase separation is responsible for the excellent physical and mechanical properties of TPU, especially elastomeric properties (Velankar and Cooper, 1998).

Various characterisation techniques that have been applied to study the microstructure of polyurethanes agree the following (Macosko, 1989; Lamba et al., 1998; and Velankar and Cooper, 1998):

1. The driving force behind the phase separation into hard and soft domains is the chemical incompatibility (polarity) and thermodynamic incompatibility (melting point) of the hard and soft segments.
2. The urethane HS forms glassy or semicrystalline polar domains with high melting point
3. The macroglycol SS forms an amorphous or semicrystalline non-polar matrix with low melting point, in which the HS are dispersed at low-to-moderate HS content.

4. The hard domains act as multifunctional crosslinking sites and reinforcing filler, resulting in material, which possesses high modulus and exhibits elastomeric behaviour.

At low temperature, T_{gSS} influence mechanical properties of polymer. At higher temperatures, either the T_g or T_m of HS determines the point at which physical crosslinks dissociate. In this case, the degree of phase separation determines whether each HS and SS will give influence on physical properties, or intermediate properties will result from some extent of phase mixing.

Factors that influence the degree of phase separation and dynamic of crystallisation in polyurethane materials include the following(Woods, 1990; Lamba et al., 1998; and Velankar and Cooper, 1998):

- Intra and inter domain interaction, especially hydrogen bonding between polymer chains
- Individual segment length, segment length distribution and overall composition
- Chemical nature, molecular weight and molecular weight distribution of SS and HS
- Polarity and crystallisability
- Mechanical and thermal history
- The nature of domain interface and mixing/dispersion of HS in SS phase.

Hydrogen bonding may occur among HS or between HS and SS. Increased phase segregation favours hydrogen bonding among HS, which is stronger than bonding between HS and SS. Hydrogen bonding does not contribute to the mechanical properties directly. However, it determines the aggregate morphology, which in turn influences the overall morphology and material properties (Lamba et al., 1998). Hydrogen bonding is stable, therefore physical properties change only slowly over normal range of operating temperature(Woods, 1990). Even and odd principle also applies: an even number of methylene groups of chain extender will give higher physical crosslink density than that of the odd, hence a higher melting temperature (T_m) due to a staggered structure(Woods, 1990).

The length of HS as a primary structure highly relies on preparation. The length increase of HS (and also SS) will increase the tendency toward phase separation(Woods, 1990). The rigidity of the hard segments exerts a strong influence on phase separation as well. An increase in HSconcentration willalso increase elastomer hardness, while higher molecular weight of polyols favours lower T_{gSS}. This is particularly important as tensile and other mechanical properties vary with hardness and depend on T_g. However, a maximum toughness is usually achieved at intermediate HS content of 40 – 50 %(Macosko, 1989).

The morphology of segmented copolymer following thermal treatment is time dependent, as the separation of the hard and soft segments is rapid compared to the ordering of the hard segments (Lamba et al., 1998). It depends on chemical composition and length of segments, and there is a critical temperature below which phase separation time increase as temperature decrease, and above which the time increase with the temperature. Above 180 °C phase mixing begin and there will be no phase separation(Macosko, 1989).

THERMAL PROPERTIES

Linear segmented TPU are very sensitive to thermal history(Saiani et al., 2001). Therefore thermal characterisation of TPU will reveal important information of the TPU structure and the influence of preparation procedure.

Koberstein and Galambos(1992) observed a dependency of thermal properties to specimen preparation procedure.Their studyon the origin of multiple melting endotherms in TPU used simultaneous synchroton X-ray and DSC. In melt-crystallised sample, multiple endotherms are associated with the melting of two distinct HS crystal populations that have different melting points. For compression mould sample, multiple melting observed at low heating rate is associated with melting-recrystallisation-melting of the extended crystalline polymorph into a new poorly organised HS structure. However, at high heating rate only a single endotherm is observed, where the crystal structure is determined to be an extended form.

A study by*Saianiet al.*(2001) using DSC also analysed the origin of multiple endotherms of TPU but with varying HS contents. They observed high temperature endothermic transitions, which are assigned to the disruption of an ordered structure that leads to a two steps of melting process:

(1) melting of the ordered structure presents in hard phase
(2) microphase mixing of the SS and HS.

It can also be concluded that T_g of hard phase increased with increasing HS content(Uhlig, 1999). The temperature difference for ordering hard phase also increased with increasing HS concentration. Sample with 65% HS content possesses a critical property, below which a homogeneous mixed phase is common, and above which samples are in two phases state. Following melt quenching no T_g of soft phase was found for this sample, but after annealing it showed the same T_g of the soft phase as for sample with 50% HS content.

Chen et al.(1998) studied the transitional endotherms for amorphous HS. They suggested that the first lower endotherm (T_1) observed at 20 – 30 °C above annealing temperature had been generally ascribed to a short-range order of unknown nature. It is an enthalpy relaxation behaviour resulting from a prolonged physical aging process. The intermediate endotherm (T_2) observed at 120 – 200 °C was attributed to a HS long-range order of unspecified nature, or the onset of microphase mixing of HS and SS. The T_2 structure would reduce the HS mobility and raise T_{gHS} in different degrees to a temperature near the vicinity of T_2. The third endotherm (T_3) occurring above 200 °C is typically attributed to the melting at the HS microcrystalline region.

Velankar and *Cooper*'s study (2000) on SS molecular weight concluded that the degree of microphase separation increased with HS block length. Qualitative observation that they performedhad revealed that the samples were non crystalline with a broad T_g at low temperature. The T_g of SS decreased with increasing SS molecular weight, due to improved microphase separation. T_g was also increased several degrees by quenching. A quantitative calculation using Couchman equation justified the qualitative conclusion and showed that the equation is only valid for high HS content at high temperature (> 100 °C). They also suggested that microphase separation analyses would give better results if DMTA or SAXS were used.

MECHANICAL PROPERTIES

O'Sickeyet al.(2002) who studied the effect of SS molecular weight and HS content of segmented polyurethane-urea (SPUU) concluded that decreasing SS molecular weight will increase and broaden T_g of SS, and also decrease and broaden the peak of $\tan\delta$. This was because of the increasing percentage of SS was restricted by the hard phase. This decrease in mobility of SS led to a less complete separation. The interfacial thickness was relatively constant regardless of SS length, with more possibility of increasing area or volume. The effect of varying HS content was seen to be minor in much of the structural analysis, in comparison to the effect of varying the SS molecular weight.

Their further study on the structure and property relationship concluded that the polyol additive acted as soft segment, as well as chain extender(O'Sickey, et al., 2002). The increase of the additive content increased T_g and modulus above T_g. The increase was higher than predicted from the behaviour of pure polyol.

According to *Adhikariet al.*(1999) who studied macrodiol-based aliphatic PU elastomer, secondary chain extenders disrupt hard segment order. Morphology was changed and transition showed dependency to the secondary chain extenders structure. At low temperature, transitions were very weak. The first transition found was glass transition of soft segment. The origin of the second or intermediate transition was not clear, but they suggested that it was more likely due to the influence of end groups.

According to some studies, a broad distribution of HS length will give lower temperature of phase mixing and poorer phase segregation resulting in lower stored/elastic modulus (E') and higher mechanical damping factor (tan δ) because of higher loss/viscous modulus (E")(Macosko, 1989). Related to a phase diagram with LCST (Lower Critical Solution Temperature), a sample with broad HS size distribution has some portion of short HS. As HS size decreases, its volume fraction also decreases. The interaction parameter (χ) then will increase, thus the temperature of mixing decreases.

MORPHOLOGICAL PROPERTIES

A study by *Garrettet al.*(2001) on the morphology of PU microdomain using AFM - tapping mode revealed that the free surface of a poly(urethane urea) mainly consists of cylindrical domains of 5-10 nm width, and up to ca. 100 nm length, with some spherical domains of ~10 nm diameter. Changes in surface morphology/domain dimension with copolymer composition were not detected. Bulk analysis of cross sectional image showed spherical domains of 10-15 nm diameters. A quantitative analysis resulted in inter domain spacing of 11-12 nm. They also suggested that varying tapping forces would give different results, for instance a higher tapping force will sense a deeper structure of HS.

A research was carried out by *Revenko et al.*(2001) on the surface structure of polycarbonate polyurethanes, with a stoichiometrically controlled mixture of soft segments. The phase mode AFM data showed that the surface of HDI polymers consisted of relatively stiff rod-like structures, which could correspond to the aggregation of the soft segments inside the polymers. The top layer appeared to be densely crystallized containing relatively higher hard segment components covering the sub-surface matrix of rod like structures. The results indicated that the microdomain structures depend on the hard segment chemistry and are relatively less dependent on the stoichiometry.

O'Sickey et al. (2002) looked at the influence of SS molecular weight and HS content of segmented polyurethane-urea (SPUU). They concluded that the increasing molecular weight of SS was shown by larger grown structure. The decrease in average SS length dramatically increased the grain size that is greater amount of hard domain.

Their further study observed a string-like superstructure, which clearly showed the presence of gelled HS(O'Sickey et al., 2002). This fact was also implied by an unexpected increase in interdomain spacing determined by SAXS. This was due to the increase in molecular weight of SS. A larger spacing between the light-coloured regions (hard phase)distinctly existed, which showed an increase in interdomain spacing. The increasing HS content increased the amount of light-coloured region seen in the image. It also made the distinction between light (hard phase) and dark regions (soft phase) appeared more clearly.

McLean and Sauer'sstudy in 1997 using real space, tapping mode AFM on nanophase morphology of polyurethane and polyamide elastomers showed a local stiffness variation of hard domains beneath a ca. 1 nm thick of SS over layer. The ca. 7 nm diameter domains were relatively symmetric and uniformly space filling. There was no macro-crystal aggregate (spherulite) exist.

Karbach and Drechsler (1999) studied morphology elucidation of TPU using four modes of AFM: Topography, Surface Potential, Force Modulation, and Contrast Phase. Topography mode showed bright particles dispersed in dark matrix, while Surface Potential mode revealed the dipole moment of dark and bright region, which were 26 debye and 250 debye respectively.By evaluating these 2 images, they concluded that the bright particles shown were the HS domain and the dark matrix was SS domain. Force Modulation mode obtained Young's modulus of HS and SS that are 10^{10} Nm^{-2} and 10^{7} Nm^{-2} respectively. It was also observed that the resonance peaks of HS were higher than that of SS at 9 kHz, but lower at 10 kHz and 10.8 kHz. This result is in good agreement with their DMTA study where there were sharp drop of E" and maxima in E' at -76 °C and 70 °C. A curve modeling of modulus against frequency then can be constructed by the principle of increasing modulus with increasing frequency or decreasing temperature. It was shown that the slope of SS curve was steeper than that of HS at the modulus step. The Contrast Phase mode showed bright mountains over dark, flat valleys and performed image matching with image from other microscopy methods.

Velankar and Cooper's (1998) study suggested that SAXS is useful for elucidating the structure of multiphase material in the size range of about 2-200 nm. Most quantitative analysis is based upon models of the morphology, which may be very detailed ones that predict specific features of the scattering curves. Most typical PUs show small-angle scattering profiles with a single peak, and the most common assumption is one of a lamellar morphology allowing at least the long spacing (interlamellar distance) to be calculated. Other morphological details such as width of interphase and microphase composition may also be calculated.

Sudaryanto and Koizumi's study in 1999 found that the existence of microphase separation results in the increase of the surface free energy, with the SS being more predominant on the surface. They also revealed that the microphase separation would be obviously observed at high HS content, i.e. > 50%. Increasing HS content gives microphase separation structure and sharp melting peak. The interdomain distance was estimated to be 19 nm for HS content of 68wt%. The decreasing HS content thus broaden or even weaken the melting endotherm peak. The microphase separation developed with increasing temperature. In this case, the interdomain distance was reduced due to enlarging domain size. Another reason may be an increase in mobility of SS that lead hard domains to move close each other. Vigorous movement of SS may also stimulate the increase in phase separation.

A study by *Koberstein et al.* (1992) on microdomain morphology of compression-moulded TPU concluded that TPU also shows behaviour of chain folded semi-crystalline polymers, in term of crystal thickening accompanied by an elevation in the melting point. Materials with high amount of HS showed HS microdomain structure that consistent with the lamellar model of Koberstein and Stein. Materials with HS content ≤40 wt% exhibited a discrete HS morphology.

Further evaluation by *Koberstein and Leung* (1992)on microphase composition of the same samples suggested that microphase compositions of pseudo-two-phase segmented block copolymer could be approached by the modified Fox equation. The value (estimated to be 5-7 residual MDIs/sequence) was then used to estimate the critical HS sequence length, below which hard sequence dissolved within SS microphase.

Lan et al.(1996) studied the synthesis and characterisation of PU with different HSs, chain extenders and SSs. According to them, to understand more thoroughly the morphological behaviour of segmented polyurethane, the kinetic effects should be considered, including viscosity of SS, interaction between HS, and HS mobility.

CONCLUSION

All researches in this field agree the significant influence of hard segment and soft segment roles in determining the physical properties of polyurethanes. Most of them study the structure-property-morphology relationship. However, only few of them studied specifically the influence of polydispersity of hard segment and its architecture. Therefore more studies are still required to reveal important information to completely understandthe microphase behaviour of TPU.

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