



Budapest University of Technology and Economics

**ROLE OF INTERACTIONS ON THE STRUCTURE
AND PROPERTIES OF SEGMENTED
POLYURETHANE ELASTOMERS**

Ph. D. Thesis

by

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1. Introduction

Segmented polyurethanes (PU) are versatile materials used in a large number of areas in industry and in our everyday life. Their properties depend on several factors and can be varied in a wide range by the proper selection of components, composition and preparation conditions. Depending on these factors polyurethanes can be cross-linked foams or linear elastomers, but they are also applied as moldings, adhesives, paints, varnishes, finishing coats, etc. Because of their advantageous properties like haemo and tissue compatibility polyurethanes are extensively used in health care mostly as medical devices. They are applied as encapsulants for hollow-fiber devices, dip-molded gloves and balloons, asymmetric membranes, functional coatings, and as extruded profiles for catheters. The selection of components, composition and reaction conditions determine phase separation and thus structure. However, the proper adjustment of properties to meet the demands of a specific application requires the extensive knowledge of structure-property correlations and the factors influencing them. The determination of these correlations and finally the control of structure is the goal of most studies in this area^{1,2}.

Arterio-venous diseases are extremely dangerous and threaten a large part of the population. Instead of open surgery these diseases are treated more and more frequently by endovascular techniques. Liquid embolizing agents are the newest materials used for the treatment. These are less invasive than earlier methods and result in high recovery ratios. A few years ago medical doctors from the University of Pécs approached the Laboratory of Plastics and Rubber Technology to join their effort in finding a polymer with optimum properties for endovascular surgery. The discussions lead to a large project resulted in a PhD thesis³, which compiled most of the scientific results obtained up to that stage. The components and the composition of the polyurethanes studied covered a wide range and we investigated various questions from polymerization kinetics, through structure-property correlations^{4,5}, to the problematic of contrasting⁶.

¹ Koberstein, J.T., Galambos, A.F., Leung, L.M. *Macromolecules* **25**, 6195-6204 (1992).

² Koberstein, J.T., Leung, L.M. *Macromolecules* **25**, 6205-6213 (1992).

³ Pukánszky, B.Jr.: *Segmented polyurethane elastomers for endovascular surgery: kinetics, properties, application*. PhD Thesis, Laboratory of Plastics and Rubber Technology, Budapest University of Technology and Economics, Budapest, 2008.

⁴ Pukánszky, B. Jr., Bagdi, K., Tóvölgyi, Zs., Varga, J., Botz, L., Hudak, S., Dóczy, T., Pukánszky, B. *Eur. Polym. J.* **44**, 2431-2438 (2008).

⁵ Pukánszky, B.Jr, Bagdi, K., Tóvölgyi, Zs., Varga, J., Botz, L., Hudak, S., Dóczy, T., Pukánszky, B. *Progr. Colloid. Polym. Sci.* **135**, 218-224 (2008).

⁶ Figyelmesi, Á., Pukánszky, B.Jr, Bagdi, K., Tóvölgyi, Zs., Varga, J., Botz, L., Hudak, S., Dóczy, T., Pukánszky, B. *Progr. Colloid. Polym. Sci.* **135**, 57-64 (2008).

Considerable knowledge was accumulated about the structure and properties of segmented polyurethane elastomers during those years. It became obvious that structure is more complicated than reported in the open literature and several questions have not been answered yet, like phase separation kinetics, the role of interactions, crystallinity etc. Detailed analysis of structure and of its dependence on the stoichiometry of the reaction mixture indicated that our linear polyurethanes have hierarchical structure consisting of several phases. Finding explanation for the sometimes contradictory observations related to structure-property correlations proved to be challenging thus research continued to answer open questions. The focus of the research shifted slowly from the solution of application oriented problems towards the more thorough characterization of structure, and latter towards the study of interactions. Several new techniques were introduced including various instrumental methods, evaluation approaches and model calculations. Nevertheless, practical aspects have not been completely forgotten, the knowledge acquired was and is used for the solution of industrial problems, and a new project have been started recently for a different medical application of some of the materials developed. This second PhD –thesis, which is a direct continuation of preceding studies, reflects both the shift in our interest and the deeper knowledge obtained during these studies. As mentioned above, the goal of the research was to obtain a deeper knowledge of structure-property correlations in linear segmented polyurethanes and about the factors affecting structure and properties in them in order to develop guidelines for the preparation of materials with desired properties.

2. Experimental

The polyurethanes studied were prepared from 4,4'-methylenebis(phenyl isocyanate) (MDI), 1,4-butanediol chain extender (BD) and a polyether or polyester polyol with a molecular mass of 1000. The polyether polyol was poly(tetrahydrofurane) (PTHF), while the polyester was poly(butanediol-adipate) (PBDA), with a functionality of 2.0. MDI was used as received, butanediol was distilled in vacuum at 190 °C, and the polyols were dried at 80 °C in vacuum for a day before the reaction. The variables changed in the various series were the ratio of the –OH and –NCO functional groups at the start of the reaction (NCO/OH ratio) and the ratio of the –OH functional groups of the polyol and that of the total diol (POH/OH ratio). The first (NCO/OH ratio) was varied between 0.90 and 1.2, while the second (POH/OH ratio) changed from 0 to 1 in 0.1 steps. One step bulk polymerization was carried out in an internal mixer (Brabender W 50 EH) at 150 °C, 50 rpm for 30 min. The polymer was compression molded into 1 mm plates at 200 °C and 5 min using a Fontijne SRA 100 machine for characterization.

In one series molecular weight was determined by gel permeation chromatography (GPC). In other series changes in molecular weight were deduced from the torque measured during reaction in the internal mixer. Measurements were done in tetrahydrofuran (THF) using a Waters 201 chromatograph with 5 UltraStyragel columns. Specific interactions were estimated by the measurement of solvent absorption. Ethanol and n-octane were used as solvents and Flory-Huggins interaction parameters were calculated from the equilibrium solvent uptake. Further information about interactions was obtained by molecular modeling. Fourier transform attenuated total reflectance infra-red spectra (FTIR-ATR) were recorded on the compression molded plates in the wavelength range of 4000 and 400 cm^{-1} . The structure of the samples was characterized also by SAXS and XRD. The morphology of smooth, cross-sectioned areas at the specimen surface was examined by AFM.

The relaxation transitions of the various structural units of the polymers were studied by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Two heating and a cooling run were done in the DSC on 10 mg samples with a rate of 20 $^{\circ}\text{C}/\text{min}$, using a Mettler Toledo TA 4000 apparatus equipped with a DSC 30 cell. DMA spectra were recorded on samples with 20 x 6 x 1 mm dimensions between -120 and 200 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C}/\text{min}$ heating rate in N_2 atmosphere using a Perkin Elmer Pyris Diamond DMA apparatus. The measurements were carried out in tensile mode at 1 Hz frequency and 10 μm deformation. Mechanical properties were determined by tensile testing on dog bone type specimens with 50 x 10 x 1 mm dimensions at 100 mm/min cross-head speed using an Instron 5566 apparatus. Shore A hardness was determined on 4 mm thick samples created by the stacking of 1 mm pieces. The transparency of the compression molded plates was measured by a Spekpol UV-VIS apparatus at 500 nm wavelength.

3. Results

In the first part of the research we studied materials prepared earlier and characterized them more in detail with various techniques. The thermal analysis of our segmented PU elastomers by DSC and DMTA measurements indicated several transitions in these polymers. The three glass transition temperatures observed were assigned to the relaxation of the aliphatic $-\text{CH}_2-$ groups of the polyol, and to that of soft and hard segments, respectively. The melting of the small amount of slightly ordered hard phase resulted in an endotherm peak. The glass transition temperature of the hard and soft phases changed with the NCO/OH ratio indicating changes in phase structure and in the composition of the phases. This latter conclusion was confirmed by the maximum observed in the number of relaxing soft seg-

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ments. Mechanical properties depended quite strongly on the stoichiometric ratio of the components. Changes in the relatively small number of chain-end functional groups resulted in considerable modification of mechanical properties. Strength is determined by molecular weight and interactions, while stiffness depends mainly on phase structure. Surprisingly enough, –OH excess yields stiffer polymers, since the interaction of the –OH groups results in a decrease in the amount of the soft phase. A close correlation was established between tensile modulus and the number of relaxing soft segments as shown in Fig. 1.

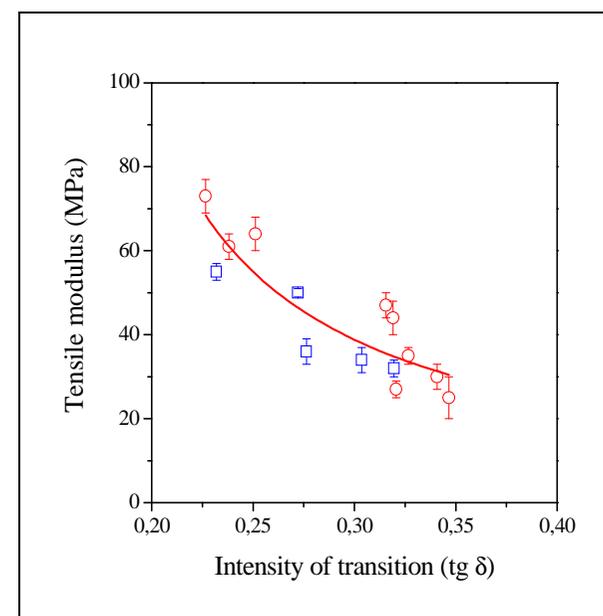


Fig. 1 Correlation between stiffness and the number of relaxing soft segments in polyether PU elastomers synthesized with different NCO/OH ratios. Symbols: (□) OH excess, (O) NCO excess.

We found that interactions govern phase structure and properties, thus they need further study and analysis. Novel quantitative AFM mechanical property mapping modes were also used for the characterization of selected samples. The observed morphology strongly depends on stoichiometric ratio and provides specific “fingerprint” phase images allowing the identification of the sample. AFM clearly resolves the elastic moduli of stiff and soft segments of phase separated polyurethane samples at nanoscale resolution (Fig. 2). Modulus values obtained

with HarmoniX Imaging and Peak Force Tapping are in very good agreement. Surface mean moduli values do not coincide with bulk values obtained via tensile testing because of fundamentally different averaging procedures and effects that lead to the respective modulus values (surface and volume averaging).

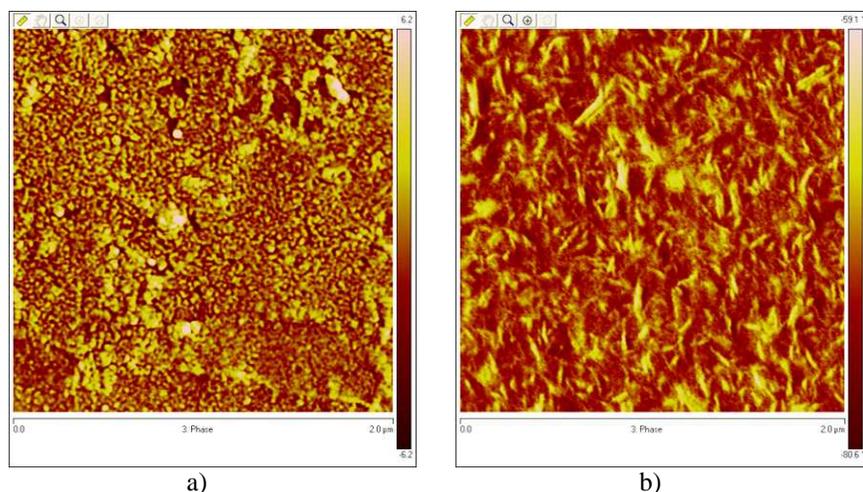


Fig. 2 AFM micrographs taken from PU samples prepared from polyester (a) and polyether (b) polyol at the NCO/OH ratio of 1.030 and 1.025, respectively. The polyester polyurethane (a) represents more homogeneous structure than its polyether counterpart (b).

Polyurethanes were prepared also from a polyester polyol. The experiments carried out as a function of changing stoichiometry proved that competitive interactions among various groups including chain-end functional groups lead to the formation of slightly ordered phases of sub-nanometer size at both ends of the composition range. These structures assemble to larger units at the 10 nm level, which further associate to even larger entities scattering light and decreasing the transparency of the samples. The order of the primary units, together with the number and size of assemblies at both higher levels, decrease as composition approaches to equimolar stoichiometry. Although interactions between hard and soft segments decrease the mobility of the latter, the amount of less ordered amorphous phase has a maximum in this range. The stiffness of the polymer is determined by the amount of this phase, while ultimate properties are influenced also by molecular weight and the strength of interactions. The incorporation of aromatic end-

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6. Publications

The Thesis based on the following papers

1. Bagdi, K., Molnár, K., Pukánszky, B.Jr., Pukánszky, B.: Thermal analysis of the structure of segmented polyurethane elastomers; relation to mechanical properties, *J. Therm. Anal. Calorim.* **98**, 825-832 (2009) (IF: 1.587).
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groups into the crystallites of the hard phase leads to the formation of larger number of strong physical cross-links resulting in high strength and deformability.

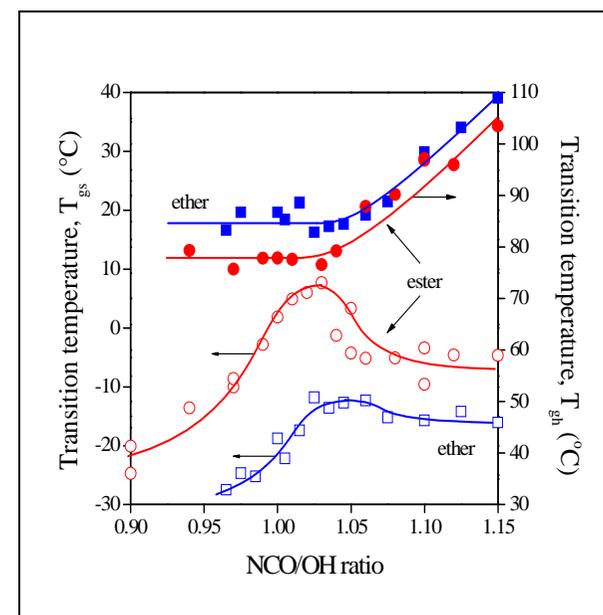


Fig. 3 Effect of polyol type and stoichiometry on the transition temperature of the phases. T_g was determined from the $t_g \delta$ traces; polyester PU soft (○) and (●) hard phase, polyether PU (□) soft and (■) hard phase.

We compared the effect of the chemical structure of the polyol on the structure and properties of the resulting polyurethane in two series of experiments. Several approaches proved that different interactions develop in polyether and polyester polyurethanes. Fourteen different specific interactions were identified in the first while 17 in the second type of polymer considering only hydrogen bonds. Estimated binding energy changes between 32 and 17 kJ/mol. The effect of interaction depends on binding energy and the number of groups participating in the formation of a certain bond. The interaction of unlike segments dominates in both types of polymers, but the relative significance of urethane-urethane bonds is smaller in polyester polyurethanes. Dissimilar interactions change the partial solubility of the phases, as well as their size and properties. Each property of the polymer is determined by a different aspect of morphology. Transparency depends on the amount of ordered hard phase, stiffness and hardness on phase composition,

while ultimate properties on stoichiometry, which determines molecular weight and the formation of physical cross-links. In the second series of experiments not the stoichiometric ratio of the functional groups, but the relative ratio of polyol/total OH was the independent variable. The comparison of two sets of polyurethane elastomers prepared with a polyester and a polyether polyol of the same molecular weight proved that specific interactions determine the phase structure and properties of these materials. Crystallinity was approximately the same in the two types of polyurethanes and the amount of relaxing soft segments was also similar. The determination of interaction parameters from solvent absorption indicated stronger interaction between hard and soft segments in the polyester than in the polyether polyurethane. The stronger interactions resulted in a larger shift of the relaxation transition of soft and hard phases towards each other in the former than in the latter polymer as shown in Fig. 3. Larger transparency of the polyester PU indicated the formation of smaller dispersed particles of the hard phase. The larger number of smaller hard phase units led to the formation of more physical cross-links distributed more evenly in the polymer. These differences in the phase structure of the polymers resulted in stronger strain hardening tendency, larger strength and smaller deformations for the polyester than for the polyether polyurethane.

4. New Scientific Results

1. By the detailed characterization of several series of segmented linear polyurethanes we confirmed earlier observations that their different properties depend dissimilarly on various factors of structure. However, we proved additionally that transparency depends on the amount of ordered hard phase, stiffness and hardness on phase composition, on the amount of soft segments, while ultimate properties on stoichiometry, which determines molecular weight and the formation of aromatic end-groups. A close correlation was found between tensile modulus and the number of relaxing soft segments.
2. We used novel quantitative AFM mechanical property mapping techniques for the first time for the characterization of segmented polyurethanes. We resolved with AFM the elastic moduli of stiff and soft segments of the phase separated polyurethane samples at nanoscale resolution.
3. We established that surface mean moduli values do not coincide with bulk values obtained via tensile testing because of the fundamentally different averaging procedures and effects that lead to the respective modulus values (surface and volume averaging). The dissimilar moduli result from the enhanced phase separation of the polymers at the surface.

4. We proved with detailed analysis carried out with a wide range of techniques that the structure of segmented polyurethane elastomers is even more complicated than widely indicated in published papers. We showed that competitive interactions among various groups including chain-end functional groups lead to the formation of slightly ordered phases of sub-nanometer size at both ends of the composition range. These structures assemble to larger units at the 10 nm level, which further associate to even larger entities in the sub-micron range scattering light and decreasing the transparency of the samples.
5. We analyzed interactions of various groups being present in segmented polyurethanes and identified fourteen different specific interactions in polyether and 17 in polyester polyurethanes considering only hydrogen bonds. We estimated binding energies which changed between 32 and 17 kJ/mol.
6. We proposed a model to take into the effect of interactions on structure development and properties of the polyurethanes studied. This effect depends on binding energy and the number of groups participating in the formation of a certain bond. We proved that the interaction of unlike segments dominates in both types of polymers, but the relative significance of urethane-urethane bonds is smaller in polyester than in polyether polyurethanes. Dissimilar interactions change the partial solubility of the phases, as well as their size and properties.
7. We proved that chain-end functional groups also participate in various interactions. Aromatic end-groups forming at NCO excess are incorporated into the ordered crystalline units of the hard phase and form physical cross-links. The number and distribution of these physical cross-link sites determines the ultimate properties (tensile strength and elongation-at-break) of the elastomers.

5. Application

As it was mentioned above this Ph.D Thesis was resulted in a large project financed by the National Bureau for Research and Development (NKTH). The goal of this research was to develop a new liquid polymer based embolizing agent for the endovascular treatment of cerebral vascular diseases. During our work we successfully synthesized a polyurethane elastomer with corresponding properties for endovascular surgery, but because of various problems the project was terminated before reaching final conclusion. Nevertheless the knowledge acquired was and is used for the solution of industrial problems, and a new project have been started recently for a different medical application of some of the materials developed.