Thermal analysis of the structure of segmented polyurethane elastomers

Relation to mechanical properties

Kristóf Bagdi · Kinga Molnár ·
Béla Pukánszky Jr. · Béla Pukánszky

Abstract Polyurethanes were prepared from 4,4′-methylenebis (phenyl isocyanate) (MDI), 1,4-butanediol (BD), and poly(tetrahydrofurane) polyether polyol (PTHF) by melt polymerization. The –OH functional group ratio of polyol/total diol was kept constant at 0.4, while the ratio of the isocyanate and hydroxyl groups (NCO/OH) changed between 0.940 and 1.150. The thermal analysis of the polymers by DSC and DMTA measurements indicated several transitions. The three glass transition temperatures observed were assigned to the relaxation of the aliphatic –CH$_2$– groups of the polyol, and to that of the soft and hard segments, respectively. The glass transition temperature of the soft and hard phase changed with the NCO/OH ratio indicating changes in phase structure and composition confirmed also by the maximum in the number of relaxing soft segments. Changes in the relatively small number of end-groups result in considerable modification of mechanical properties. Strength is determined by molecular mass 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 unique correlation was found between tensile modulus and the number of relaxing soft segments.

K. Bagdi · K. Molnár · B. Pukánszky Jr. · B. Pukánszky (✉)
Laboratory of Plastics and Rubber Technology, Department
of Physical Chemistry and Materials Science, Budapest
University of Technology and Economics, P.O. Box 91, H-1521
Budapest, Hungary
e-mail: bpukanszky@mail.bme.hu

K. Bagdi · K. Molnár · B. Pukánszky Jr. · B. Pukánszky
Institute of Materials and Environmental Chemistry, Chemical
Research Center, Hungarian Academy of Sciences, P.O. Box 17,
H-1525 Budapest, Hungary

Introduction

Polyurethanes are versatile polymeric materials playing a vital role in many industries, because their structure and properties can be varied in a wide range [1]. They are used as hard foams for thermal insulation in the building industry and in appliances, elastic foams as car seats, and furniture components, while linear elastomers as shoe soles or medical devices [1]. In this latter field they are used as encapsulants for hollow-fiber devices, dip-molded gloves and balloons, asymmetric membranes, functional coatings, and as extruded profiles for cardiovascular catheters [2, 3]. Segmented polyurethane elastomers are composed of linear molecules the properties of which depend mostly on molecular mass and on the chemical structure of the polyol [4–8]. These materials are usually prepared from an aliphatic or aromatic isocyanate, a diol or amin chain extender and a polyether or polyester polyol [9–11]. Because of the chemical dissimilarity of the components and as a result of competitive interactions, linear PU elastomers usually phase separate into hard and soft phases [12–14]. The extent of phase separation and the size as well as properties of the phases are determined by thermodynamic [15] and kinetic [16] factors. The latter are related to molecular mass and preparation conditions, while the former to composition [17]. As a result of phase separation, the properties of these polymers are not determined only by molecular mass and composition, but also by phase structure [18, 19].

In a previous communication, we showed that changing stoichiometric ratio of the functional groups modifies molecular mass as expected, but the phase structure of the polymer also changes considerably [20]. The extent of phase separation, as well as the size and properties of the dispersed phase depend very much on composition [21]. Each property of the polymer is affected differently by molecular mass and phase structure. Melt viscosity depends mostly on the length of the molecules [22], ultimate tensile properties are influenced also by interactions [23, 24], while stiffness is determined almost exclusively by phase structure [25].

The main goal of this paper was to analyze the structure of segmented polyurethane elastomers on the molecular and supermolecular level by thermoanalytical measurements. We tried to relate the mechanical properties of the polymers to their structure and identify the most important moieties which determine properties. Differential thermal calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were used for the characterization of the samples, but supplementary measurements were also carried out to support conclusions drawn from thermal data.

Experimental

The polyurethanes studied were prepared from 4,4′-methylenebis(phenyl isocyanate) (MDI), 1,4-butanediol chain extender (BD), and poly(tetrahydrofurane) polyether polyol (PTHF) with a molecular mass of 1000. The molecular structure of a repeat unit of the polymer is shown in Scheme 1. All three ingredients were purchased from Sigma–Aldrich and used as received. The –OH functional group ratio of polyol/total diol was kept constant at 0.4 in all experiments. The ratio of the isocyanate and hydroxyl groups (NCO/OH) changed between 0.940 and 1.150 resulting in almost constant mass ratios of 0.46/0.54 of the hard and the soft segments. Polymerization was carried out by melt reaction in a Brabender W 50 EHT internal mixer 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. The molecular mass of the samples was determined by gel permeation chromatography (GPC); the results have been reported earlier [19]. The change of molecular mass on stoichiometry follows theoretical predictions and it is an almost symmetrical function of composition.

The transitions of the various structural units were studied by differential scanning calorimetry (DSC). Two heating and a cooling runs were done on 5–10 mg samples in N_2 atmosphere with a heating or cooling rate of 20 °C min^{-1} between −120 and 250 °C using a Mettler Toledo TA 4000 apparatus equipped with a DSC 30 cell. Mostly data recorded in the first heating run are used for evaluation here, because phase structure depended also on the thermal history of the samples. Dynamic mechanical spectra (DMTA) were recorded on samples with $20 \times 10 \times 1$ mm^3 dimensions cut from compression-molded plates between −120 and 200 °C at 2 °C min^{-1} heating rate in N_2 atmosphere in tensile mode using a Perkin Elmer Pyris Diamond DMA apparatus. The structure of the samples was characterized also by XRD using a Phillips PW 1830/PW 1050 equipment with CuK$_\alpha$ radiation at 40 kV and 35 mA in reflection mode. Mechanical properties were determined by tensile testing on dog bone type specimens with $50 \times 10 \times 1$ mm^3 dimensions at 100 mm min^{-1} cross-head speed using an Instron 5566 machine. Tensile strength and elongation-at-break were derived from recorded force versus elongation traces, while tensile modulus was determined from the initial, linear section of the traces.

Results and discussion

The results are presented in three sections. First the various structural units and their relaxation behavior are identified, then the role of these units in phase separation and the relative amount of the phases are discussed subsequently. In the last section of the paper we try to find correlation between structure and properties and identify the most important structural units determining properties by taking into account the possible interaction of functional groups.

Molecular structure, transitions

Thermal characterization offers information about the number and characteristics of structural units constituting a polymer. Three traces recorded during the first heating of the samples in the DSC cell are presented in Fig. 1 for polyurethanes prepared at different stoichiometric ratios. The NCO/OH ratio increases from the bottom to the top. Three transitions can be certainly observed on the traces. A pronounced glass transition appears at around −40 °C and

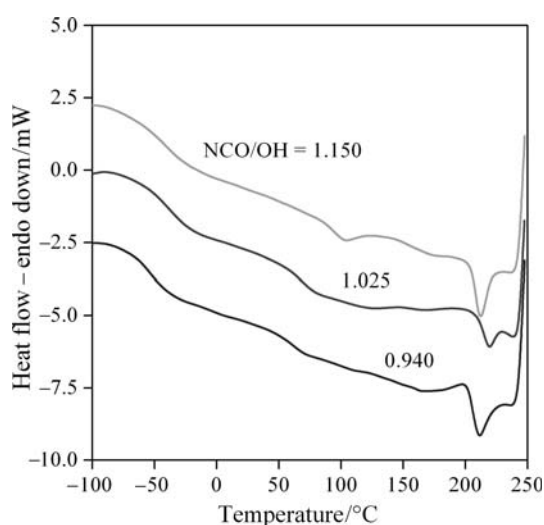**Scheme 1** Chemical structure of a repeat unit of the polymer
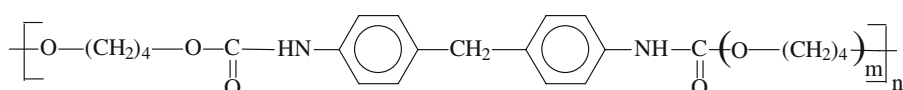
Fig. 1 DSC traces of segmented PU elastomers prepared with different NCO/OH ratios

Fig. 2 Typical DMTA spectra recorded on a segmented PU elastomer. The stoichiometric ratio of the components is 1.0

another one at higher temperature, at around 80 °C. At very high temperature, above 200 °C a melting peak also can be detected on the traces.

Glass transitions result from the relaxation of different structural moieties in the polymer. The components have separate transitions in immiscible blends, and the same happens for phase-separated block copolymers. Segmented polyurethanes are known to phase separate [1, 9, 17, 26–28]. The two glass transitions correspond to the relaxation of the hard segments formed from the isocyanate and the butanediol chain extender and to that of the soft segments consisting of the PTHF polyol, respectively. Both transitions seem to shift toward higher temperatures with increasing NCO/OH ratio.

Hard segments usually form densely packed regular structures close to a crystalline order [29]. The endotherm peak observed at around 210 °C can be assigned to the melting of this structure [30]. The position and intensity of this peak are very irregular; do not show any tendency as a function of composition. Moreover, the melting peak changes drastically with thermal history; it can be hardly detected in the second heating run. In order to determine the amount and characteristics of the ordered phase, WAXS measurements were also carried out on all samples. The analysis of the diffractograms (not shown) proved that the hard phase has some order indeed, but it is very limited and does not change much with composition. The characteristics of the ordered phase could not be determined from the traces either, because of this low regularity.

The DMTA traces of the PU elastomer prepared with equimolar NCO/OH ratio are shown in Fig. 2. The results are typical, the measurements resulted in spectra with similar characteristics for all polymers. Three transitions can be detected also on the DMTA, but these differ
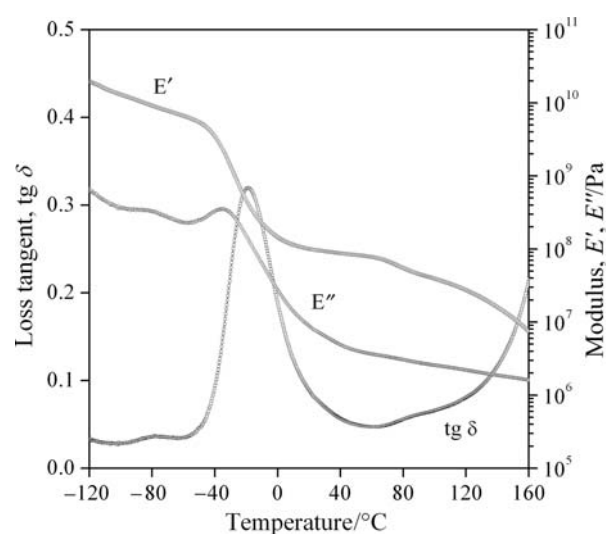
somewhat from those determined with DSC. A transition with small intensity appears at around −80 °C, which was assigned earlier to the relaxation of the –CH$_2$– units of the polyol [20]. A very intense transition dominates the spectra at around −20 °C, which must be related to the movement of the soft segments [31]. The considerable intensity of this transition results from the large change in the mobility of the soft segments as temperature crosses the T_g. Another weak transition is detected at a higher temperature, at around +85 °C, which can be assigned to the relaxation transition of the hard segments [32]. The small intensity of the transition results from the stiffness of the hard segments, their mobility is not very different below and above the transition temperature. The temperature of these transitions does not agree completely with that determined by DSC, but the differences can be explained adequately with different sample size, heating rate, and loading conditions. The melting endotherm detected at high temperature by DSC cannot be seen on the DMTA traces. The samples loose their integrity at significantly lower temperatures, which also supports the conclusions drawn from the WAXS analysis that the amount and regularity of the ordered phase are very limited.

Naturally, the location and intensity of the transitions determined by DMTA also depend on composition. Three spectra are presented in Fig. 3 as an example. Only tg δ traces are shown to facilitate comparison. The position of the peak related to the transition of the soft segment changes, a maximum seems to exist in the glass transition temperature of the soft phase. Even more surprising is the dependence of the intensity of the transition on composition, which is much larger at around the stoichiometric ratio of the components than at the extremes of the composition range. Apparently the amount of relaxing species
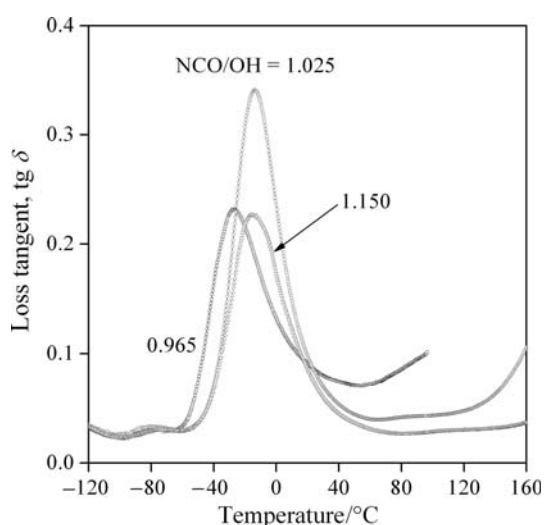
Fig. 3 Changes in the position and intensity of the relaxation transition of the soft segments on the stoichiometric ratio of the components

Fig. 4 Effect of the relative ratio of the components on the glass transition temperature of the soft and hard segments, respectively. T_g was determined from storage modulus

increases around equimolar composition and decreases as the relative amount of either component increases. All these changes must be related to the phase separation of the soft and hard segments as well as to the interaction of their various functional groups.

Phase composition and properties

The glass transition temperature of polymers depends on the mobility of the relaxing species and changes in T_g with composition are influenced also by the interaction of the corresponding phases, by their mutual miscibility. The dependence of the T_g of the two phases of our segmented PU elastomers is plotted against the stoichiometric ratio of the components in Fig. 4. The glass transition temperature of the soft segments seems to go through a slight maximum around the equimolar ratio of the components. This was explained earlier with the decreasing mobility of the soft segments with increasing isocyanate content followed by the increased exclusion of the PTHF segments from the hard phase at larger NCO excess [20]. On the other hand, the T_g of the hard phase increases continuously, but not linearly, with increasing NCO content. The non-linear dependence of the T_g of both phases on composition indicates changes in phase structure and interactions with changing NCO/OH ratio. A similar picture is obtained if we plot glass transition temperatures determined by DSC against composition, but with a larger scatter of the points around the general trend. The complementary nature of the two measurements is shown by the relatively close correlation of the T_g values determined by the two methods for the soft segments (Fig. 5). The general tendency is clear, in spite of the relatively large scatter of the measured values especially at large NCO content.
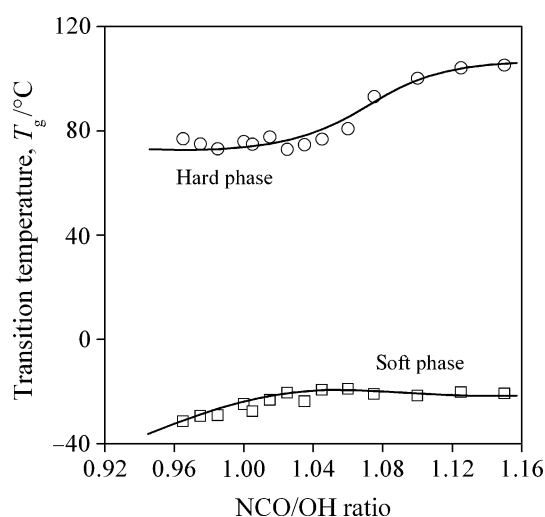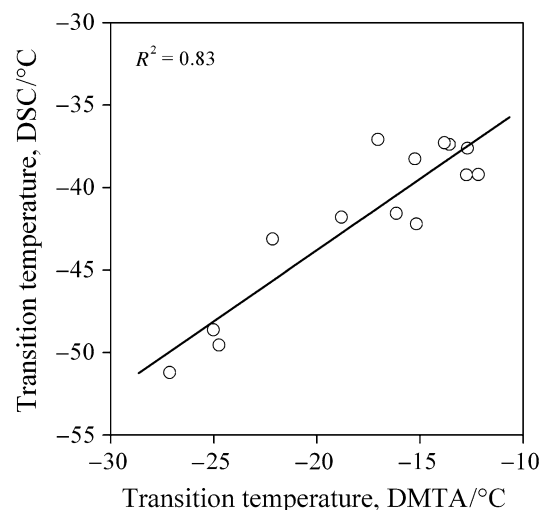

Fig. 5 Correlation of glass transition temperatures determined by DSC and DMTA, respectively, for the soft segments

The maximum in the T_g of the soft phase as well as the changing intensity of this transition with composition (see Fig. 3) indicated changes in the composition of the phases with changing stoichiometric ratio of the components. These relations are demonstrated well by Fig. 6, in which the intensity (height of the tg δ peak) of the relaxation transition of the soft segments is plotted against composition. A maximum appears at around equimolar stoichiometry indicating a maximum in the number of relaxing species in this composition range. This is somewhat surprising and seems to be in contradiction with the fact that the T_g of the soft phase also has a maximum in this range, i.e., the mobility of the soft segments is the smallest, their movement is the most restricted here. Obviously phase
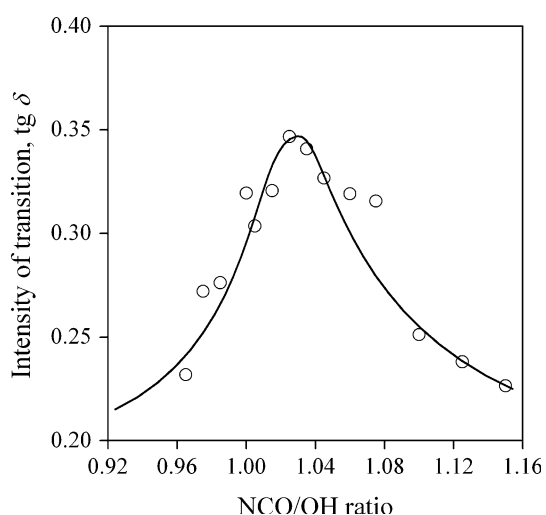
Fig. 6 Relaxation intensity of the soft segments plotted against the stoichiometric ratio of the components

Fig. 8 Changes in tensile strength as a function of the stoichiometric ratio of the components

separation is the smallest, and the mutual miscibility of the phases the largest, around this composition. This observation is strongly supported by changes in the transparency of the samples, which has similar composition dependence (not shown) as that of the intensity of soft-segment transition. We may ask the question how changing phase separation and the composition of the phases influence the mechanical properties of the polymer.

Structure–property correlations

The composition dependence of tensile modulus is presented in Fig. 7. The stiffness of the samples changes linearly with composition at both sides of the equimolar
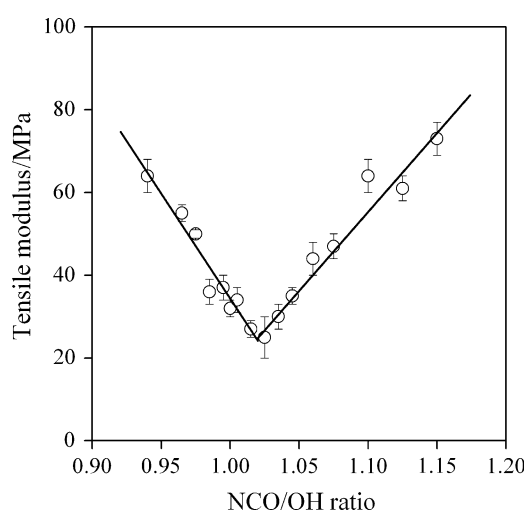

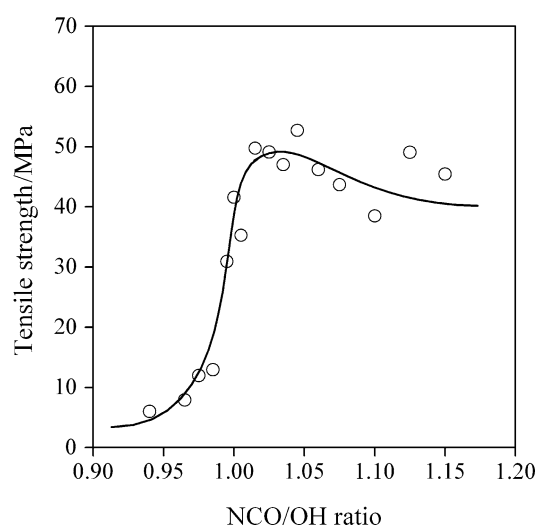**Fig. 7** Dependence of the stiffness of polyurethane elastomers on the NCO/OH ratio

stoichiometric ratio with a minimum in the middle. On the other hand, tensile strength shows a completely different dependence on composition (Fig. 8). The correlation is lopsided, strength being small at OH excess while significantly larger at high isocyanate content. Elongation-at-break shows a similar dependence on the NCO/OH ratio as strength (not shown). The different dependence of properties on composition was explained earlier by the dissimilar effect of various factors on them [20]. Modulus was shown to depend solely on phase structure, while strength is influenced both by molecular mass and interactions. Although this explanation seems to be true and it is supported by experimental evidence, the effect of the different factors (molecular mass, the number of various functional groups, interactions, phase separation, composition and amount of the phases) on properties is still not completely clear.

Polyurethanes contain a considerable number of functional groups (urethane, ether, hydroxyl, and amine end-groups) and several active hydrogen atoms which are capable of forming hydrogen bridges. The competitive interactions of these groups govern phase separation, as well as the composition and properties of the phases. The concentration of the urethane groups is large, around 2.85 mmol g^{-1}, and fairly constant throughout the concentration range. On the other hand, the number of both end-groups, i.e., –OH and –NH$_2$, forming at the two sides of the composition range is much smaller, between 0 and 0.5 mmol g^{-1}, and changes considerably with the NCO/OH ratio. As a consequence, end-groups seem to determine changes in phase structure in spite of their smaller number. Tensile modulus is plotted against the concentration of end-groups, –OH or –NH$_2$, respectively, in Fig. 9; it is fairly obvious that end-groups determine the stiffness of

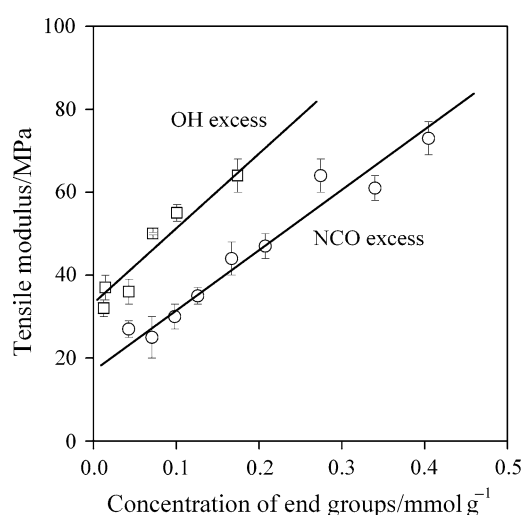**Fig. 9** Tensile modulus plotted against the concentration of end-groups formed in the polymer

Fig. 10 Effect of end-group concentration on the tensile strength of the elastomer samples

the polymer. On the other hand, the larger stiffness of samples having –OH excess is rather surprising; we would expect larger stiffness on the other end of the composition range due to the larger number of amine groups and stronger interactions.

The dependence of strength on the concentration of end-groups is completely different, as expected (Fig. 10). As mentioned above the dominating factors here are molecular mass and interactions . The strength of the samples with –OH excess is small and decreases strongly with increasing number of –OH end-groups. Obviously, the effect of decreasing molecular mass dominates changes. On the other hand the stronger interaction of the –NH$_2$ groups with the urethane groups (32 kJ mol^{-1}) compared to the –OH-urethane interaction (26–28 kJ^{-1} mol) results in much larger strength and a weaker dependence on molecular mass. Obviously, competitive interactions, phase structure, and composition, all change with the stoichiometric ratio of the components.

In order to check the effect of stoichiometry on phase structure, the intensity of the relaxation of the soft phase, i.e., the number of relaxing soft segments, was plotted against the concentration of end-groups in Fig. 11. Very close linear correlations were obtained supporting again our assumption that changing ratio of the reactants modifies phase structure and the composition of the phases. The figure explains also the apparent contradiction of larger modulus for polymers with a larger concentration of chain-end –OH groups. The interaction of the –OH groups with each other and/or with the large number of urethane groups present decreases the number of relaxing soft segments and thus increases stiffness. Since the opposite occurs on the other side of the composition range, i.e., at isocyanate
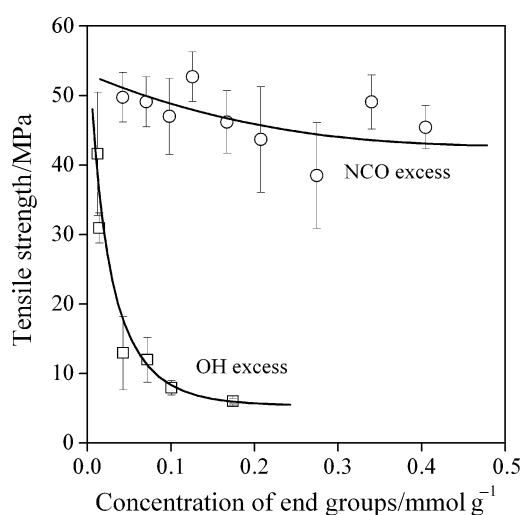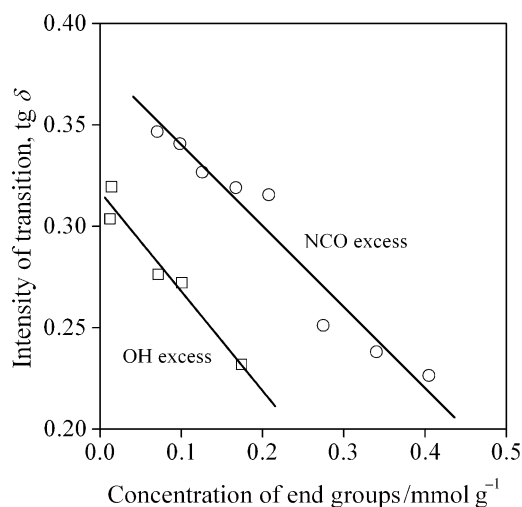

Fig. 11 Dependence of the intensity of soft-segment transition on the concentration of the end-groups formed

excess, the soft segments are excluded from the hard phase, which result in less stiff polymers. This explains also the slight maximum in the T_g of the soft phase, phase separated soft segments are more mobile than those interacting with hard segments. Accordingly, the extent of phase separation and the amount of flexible molecules determine the stiffness of the elastomer samples. This conclusion is confirmed completely by Fig. 12, in which tensile modulus is plotted against the intensity of the transition of the soft phase. A very good linear correlation is obtained indicating that stiffness depends basically only on phase structure and composition, and particularly on the amount of mobile soft segments. Phase separation and the properties of the phases
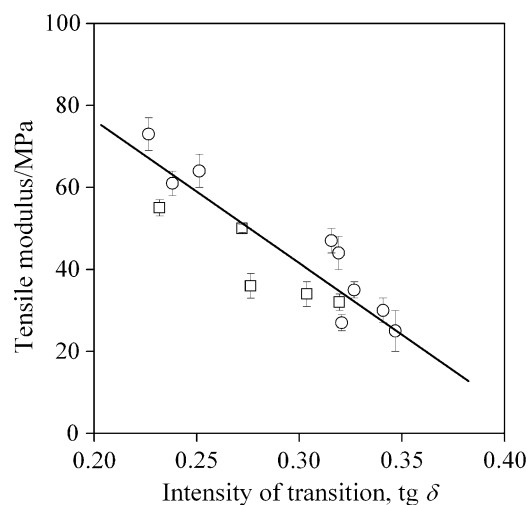
Fig. 12 Linear correlation between stiffness and the number of relaxing soft segments. *Square* OH excess, *Circle* NCO excess

are determined by competitive interactions which need further study and analysis.

Conclusions

The thermal analysis of 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 $-CH_2-$ 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 segments. Mechanical properties depend quite strongly on the stoichiometric ratio of the components. Changes in the relatively small number of chain-end functional groups result in considerable modification of mechanical properties. Strength is determined by molecular mass 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 unique correlation was found between tensile modulus and the number of relaxing soft segments. Interactions govern phase structure and properties, thus they need further study and analysis.

References

1. Randall D, Lee S, editors. The polyurethanes book. New York: Wiley; 2002.
2. Bártolo P, Bidanda B. Bio-materials and prototyping applications in medicine. New York: Springer; 2008.
3. Lamba NMK, Woodhouse KA, Cooper SL. Polyurethanes in biomedical applications. Boca Raton: CRC Press; 1997.
4. Guelcher SA, Gallagher KM, Didier JE, Klinedinst DB, Doctor JS, Goldstein AS, et al. Synthesis of biocompatible segmented polyurethanes from aliphatic diisocyanates and diurea diol chain extenders. Acta Biomater. 2005;1:471–4.
5. Wiggins MJ, MacEwan M, nderson JM, Anne H. Effect of soft-segment chemistry on polyurethane biostability during in vitro fatigue loading. J Biomed Mater Res A. 2004;68A:668–83.
6. Bajsic EG, Rek V, Sendijarevi A, Sendijarevit V, Frish KC. The effect of different molecular weight of soft segments in poly-urethanes on photooxidative stability. Polym Degrad Stab. 1996;52:223–33.
7. Furukawa M, Shiiba T, Murata S. Mechanical properties and hydrolytic stability of polyesterurethane elastomers with alkyl side groups. Polymer. 1999;40:1791–8.
8. Kim H-D, Lee T-J, Huh J-H, Lee D-J. Preparation and properties of segmented thermoplastic polyurethane elastomers with two different soft segments. J Appl Polym Sci. 1999;73:345–52.
9. Macosko CW. RIM, fundamentals of reaction injection molding. Munich: Hanser; 1989.
10. Jasińska L, Haponiuk JT, Balas A. Dynamic mechanical properties and thermal degradation process of the compositions obtained from unsaturated poly(ester urethanes) cross-linked with styrene. J Therm Anal Calorim. 2008;93:777–81.
11. Lin B, Yang L, Dai H, Hou Q, Zhang L. Thermal analysis of soybean oil based polyols. J Therm Anal Calorim. 2009;95:977–83.
12. Ayres E, Oréfice RL, Yoshida MI. Phase morphology of hydro-lysable polyurethanes derived from aqueous dispersions. Eur Polym J. 2007;43:3510–21.
13. Miller JA, Speckhard TA, Cooper SL. Monte Carlo simulation study of the polymerization of polyurethane block copolymers. 2. Modeling of premature phase separation during reaction using the two-phase ideal reaction model. Macromolecules. 1986;19: 1568–74.
14. Stanford JL, Still R, Wilkinson A. Effects of soft segment pre-polymer functionality on structure development in RIM copolymers. Polymer. 1995;36:3555–64.
15. Kang W, Stoffer JO. Effect of hard segments on morphology of polyurethanes. Polymer Prepr. 2000;41:1132–3.
16. Chu B, Gao T, Li Y, Wang J, Desper CR, Byrne CA. Microphase separation kinetics in segmented polyurethanes: effects of soft segment length and structure. Macromolecules. 1992;25:5724–9.
17. Król P. Synthesis methods, chemical structures and phase structures of linear polyurethanes properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers. Prog Mater Sci. 2007;52:915–1015.
18. Zhou Q, Zhang L, Zhang M, Wang B, Wang S. Miscibility, free volume behavior and properties of blends from cellulose acetate and castor oil-based polyurethane. Polymer. 2003;44:1733–9.
19. Skarja GA, Woodhouse KA. Structure-property relationships of degradable polyurethane elastomers containing an amino acid-based chain extender. J Appl Polym Sci. 2000;75:1522–34.
20. Pukánszky B Jr, Bagdi K, Tóvölgyi Zs, Varga J, Botz L, Hudak S, et al. Nanophase separation in segmented polyurethane elastomers:

effect of specific interactions on structure and properties. Eur Polym J. 2008;44:2431–8.

21. Sánchez-Adsuar MS, Pastor-Blas MM, Martin-Martinez JM. Properties of polyurethane elastomers with different hard/soft segment ratio. J Adhes. 1998;67:327–45.

22. Colby RH, Fetters LJ, Graessley WW. The melt viscosity-molecular weight relationship for linear polymers. Macromolecules. 1987;20:2226–37.

23. Kovacevic V, Lucic S, Cerovecki Z. Influence of filler surface pre-treatment on the mechanical properties of composites. Int J Adhes Adhes. 1997;17:239–45.

24. Pukanszky B. Influence of interface interaction on the ultimate tensile properties of polymer composites. Composites. 1990;25:255–62.

25. Kojio K, Nakashima S, Furukawa M. Microphase-separated structure and mechanical properties of norbornane diisocyanate-based polyurethanes. Polymer. 2007;48:997–1004.

26. Król P, Pilch-Pitera B. Phase structure and thermal stability of crosslinked polyurethane elastomers based on well-defined prepolymers. J Apply Polym Sci. 2007;104:1464–74.

27. Velankar S, Cooper SL. Microphase separation and rheological properties of polyurethane melts. 1. Effect of block length. Macromolecules. 1998;31:9181–92.

28. Garrett JT, Xu R, Cho J, Runt J. Phase separation of diamine chain-extended poly(urethane) copolymers: FTIR spectroscopy and phase transitions. Polymer. 2003;44:2711–9.

29. Chen TK, Chui JY, Shieh TS. Glass transition behaviors of a polyurethane hard segment based on 4,4′-Diisocyanatodiphenylmethane and 1,4-Butanediol and the calculation of microdomain composition. Macromolecules. 1997;30:5068–74.

30. Frick A, Rochman A. Characterization of TPU-elastomers by thermal analysis (DSC). Polym Test. 2004;23:413–7.

31. Crawford DM, Bass RG, Haas TW. Strain effects on thermal transitions and mechanical properties of thermoplastic polyurethane elastomers. Thermochim Acta. 1998;323:53–63.

32. Chen TK, Shieh TS, Chui JY. Studies on the first DSC endotherm of polyurethane hard segment based on 4,4′-Diphenylmethane Diisocyanate and 1,4-Butanediol. Macromolecules. 1998;31:1312–20.