New approach to evaluate microphase separation in segmented polyurethanes containing carbonate macrodiol

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A B S T R A C T

The solid state properties of segmented polyurethanes (TPU) are determined to a great extent by their microphase-separated structure thus making them attractive for several technological applications. In addition to microphase separation, hydrogen bonding and partial crystallization of the soft segments often contribute to the thermoplastic elastomeric behavior of TPUs. In this work, we applied infrared spectroscopy to determine the degree of microphase separation and quantitative analysis of H-bonds formation between functional groups of hard and soft segments in poly(carbonate-urethane)s (PCUs) with a narrow weight ratio from 35 to 41 wt% of hard segments. Using the Gaussian deconvolution of infrared spectroscopy peaks we determined the degree of microphase separation in synthesized PCUs, indicating for the first time, the significant contribution of the H-bonds present in mixed phase of hard and soft segments. Moreover, high content of mixed phase and additional physical carbonyl groups interactions of carbonate macrodiol resulted in the highest elastic modulus for PCU containing only 41 wt% of hard segments. The results demonstrated that the newly introduced deconvolution formula and detailed analysis of infrared spectra are a precise tool in determining the degree of microphase separation in segmented polyurethanes even at narrow segments ratio.

1. Introduction

Thermoplastic polyurethanes (TPUs) belong to the group of thermoplastic elastomers (TPE), and their properties can be tailored ranging from soft rubber-like materials to hard and stiff polymers. The TPUs which are linear, random segmented copolymers, consist of continuous soft segments (SS) matrix and hard segments (HS) domains. Mainly, the diisocyanates and chain extenders are forming the HSs, while SSs are built by macrodiols such as oligoesters, ethers or more recently carbonates [1]. The TPUs' unique properties are a consequence of thermodynamic incompatibility of segments leading to a microphase separation and formation of a discrete micro (or nano) domain structure [2–6].

In general, the microphase separation is influenced by the characteristics of polymeric building blocks (segments) such as miscibility, length, chemical composition and weight ratio [7–9]. Several methods can be used to evaluate the degree of microphase separation (DPS), including the calculations based on mixing theory (determination of the Gibbs' free enthalpy of mixing), calorimetric measurements (evaluation of phase transition temperatures) and spectroscopic techniques. The last one is particularly useful for evaluation of hydrogen bond interactions which are present in segmented polyurethanes, especially in hard domains. Particularly, the absorption frequency shifts are evidence of strains and stresses occurring in hydrogen bonds between different functional groups
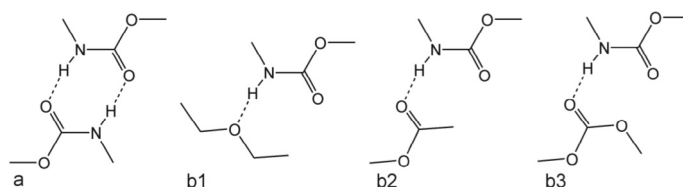

Fig. 1. Hydrogen bonds (dash line) occurring between two hard segments (a) and between hard-soft segments in segmented polyurethanes (b1, b2, and b3).

[10–12]. Several methods for DPS evaluation and/or calculation have been proposed based on spectroscopic analysis. Most of the concepts [13,14] assume that hydrogen bonded components occur in hard domains (between two urethane groups, U-U), while the unbonded ones are dispersed in the soft phase matrix. The DPS then is described by the ratio of the integrated absorbance of hydrogen bonded groups (A_{bonded}) and the sum of all groups (A_{tot}):

$$DPS = A_{bonded}/A_{tot} \tag{1}$$

Although the DPS value is related only to the hydrogen bonded and unbonded urethane groups, the overall bulk properties of segmented polyurethanes are consequence of all hydrogen bonds present in mixed, soft and hard phase. The hydrogen bonds in segmented polyurethanes are formed between −NH group (a proton donor) and oxygen (a proton acceptor) either from a carbonyl group of the urethane bond (hard segments) (Fig. 1a) or from the oxygen present in ether (Fig. 1b1), ester (Fig. 1b2) or carbonate soft segments (Fig. 1b3).

Those competitive hydrogen bonds (Fig. 1, b1-b3) are responsible for the increased amount of mixed phase and the relatively low DPS of polyurethanes, thus affecting thermal and mechanical properties. Moreover, the H-bonds formed between urethane and other functional groups, included in 'unfavorable' mixed phase, can be preferentially created due to the two-fold lower bond energy. As presented by Yilgör et al. [12], urethane–ether, and urethane–ester hydrogen bonds energies are 23.6 and 25.6 kJ/mol, respectively, whereas for urethane–urethane bond is 46.5 kJ/mol. Since the carbonate oligomers are recognized to improve the bulk properties of polyurethanes, e.g. thermal and mechanical stability, resistance to oxidation, hydrolysis, ultraviolet light, etc. [15], more detailed analysis of phase separation of such carbonate based materials is needed.

Therefore, the aim of this work was to investigate the microphase separation and its influence on thermal and mechanical properties of carbonate based polyurethanes with a narrow weight ratio of hard to soft segments. The previously published literature discuss the microphase separation of poly(carbonate-urethane)s and their properties taking into account broad segmental composition ranges [16,17]. However, a profound investigation about the influence of the hydrogen bonds and dipole-dipole interactions arising from carbonate macrodiol, as well as of slight changes in segmental composition on the microphase separation and in consequence, on the thermal and mechanical properties of thermoplastic polyurethanes are not provided in those studies. Therefore, in this work, we focus on materials with a narrow segmental composition range (from 35 to 41 wt% of HS). Quantitative analysis was carried out for synthesized PCUs in order to assess the formation of hydrogen bonding (H-bonding) occurring between urethane groups and urethane and carbonate groups. Furthermore, to determine the degree of microphase separation of the PCUs, we proposed a detailed deconvolution analysis with respect to newly defined hydrogen bonds and dipole–dipole interactions experimentally determined for the carbonate macrodiol.

2. Materials and methods

2.1. Materials

Poly(carbonate urethanes)s (PCU) were synthesized using a hydroxyl-terminated aliphatic carbonate macrodiol (CM), Desmophen C 2200 with molecular mass of 2000 mol/g, kindly supplied by Bayer Material Science and with the following characteristics: OH value, 56.1 ± 6.6 mg KOH/g; max. water content, 0.1%; viscosity at 75 °C, 2050 ± 750 mPa s; glass transition temperature, −55 °C; melting temperature, 50 °C; main component, 1,6-hexanediol. 4,4′-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD) were purchased from Sigma Aldrich (Poznan, Poland), ammonia aqueous solution (25%) and dimethylformamide (DMF) were purchased from ChemPur (Piekary Slaskie, Poland).

2.2. Synthesis of poly(carbonate urethane)s

The poly(carbonate urethane)s were synthesized without any catalyst, via one-step bulk polymerization with narrow segmental composition range: hard segment content was 35, 37, 39, and 41 wt%, respectively. First, Desmophen C 2200 was melted and then dried under reduced pressure at 120 °C for 0.5 h. Next, BD was added to the macrodiol and the mixture was stirred for 5 min, after that the diisocyanate was dissolved into the diols mixture by vigorous stirring. After homogenization, the reaction mixture was transferred into a mold and allowed to react at 120 °C for 2 h. The molar ratios of the reagents and the hard segment content of the four synthesized polyurethanes are shown in Table 1. The hard segment content by weight, *wt(%)HS*, was calculated as follows:

$$wt(\%)HS = \frac{nM_{MDI} + nM_{BD}}{(n+1)M_{MDI} + nM_{BD} + nM_{CM}} \times 100\% \tag{2}$$