Two-domain morphology in viscoelastic polyurethane foams

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ABSTRACT

The morphology of viscoelastic polyurethane (PU) foams is examined and compared with flexible, elastic PU foam. Hard and soft domains for both foam types are found with atomic force microscopy, with good signal to noise. TD-NMR spectroscopy is sensitive to the presence of multiple phases through the contrast in the segmental mobility of the domains. Results on the viscoelastic foams, as with the flexible foams, indicate two-phase morphology, contrary to the conventional wisdom in the industry that viscoelastic polyurethane foams are phase-mixed. Segmental mobility is correlated to tan delta at the experimental temperature. The segmental mobility of the soft domain is correlated to the viscoelastic recovery time of the memory foams. The example of viscoelastic foams demonstrate the detection sensitivity of TD-NMR, where domains with similar composition/density but different mechanical strength are distinguished through segmental mobility contrast.

1. Introduction

The physical and mechanical properties of polyurethanes (PU) are highly influenced by the microstructural ordering of those materials. Oftentimes, an underlying assumption is that the hard segment generated through the urea ("blowing") reaction yields a completely phase separated morphology so that the hard domain is composed purely of hard segments. A previous modeling effort by Ginzburg et al. has used this assumption to predict PU foam properties from the formulation, and the results are relatively valid in the case of elastic PU foams [1]. In the case of viscoelastic ("Visco") PU foams, modeling has generally been more challenging. This is partly because as the average lengths of the blocks in the polymer becomes shorter, which is the case for both hard and soft segments in Visco systems, component solubility and the block lengths strongly influence phase separated morphology [2]. Thus, accurate *a priori* determination of the system phase becomes difficult. Visco foams are used as high-end shape memory foams in the mattress industry and accounts for about 30% of the PU slab-stock foam market [3]. Polyurethane Visco foams have also been considered as a viable scaffold material for new biomaterials [4]. Visco foams made partially from plant derived polyols are available, and have been studied in the past [5,6], although they are not widely used in the bedding industry. The practical relevance of this type of fundamental investigation is high.

Commonly used polymer characterization tools such as DMA, SAXS, and DSC have been useful in the study of polyurethanes (PU) [7—9], and have been sensitive to the phase separated morphology that exists in flexible, elastic ("Flex") foams, owing to the blocky segmented chain architecture [10]. In the case of Visco foams, because of both higher hydroxyl content in the polyol and higher water content, the chain architecture is less blocky, leading to a poorly defined phase morphology that has often been identified as phase-mixed [11—13]. Atomic force microscopy (AFM) is capable of detecting phase domains on the order of nanometers in size. This technique has been used frequently to probe well phase separated systems such as block copolymers [14—16], including polyurethanes [17—19] and is applied to the study of Flex and Visco polyurethane foams.

Time-domain nuclear magnetic resonance (TD-NMR) spectroscopy is capable of characterizing hard domains and soft domains, with low and high segmental mobility, respectively, in polyurethane foams. TD-NMR can be used to identify and quantify any two (or more) components or domains with sufficiently contrasting segmental mobility [20,21]. The same type of technique has been used to measure fat-to-moisture content in food [22—24], and to study semicrystalline polymers such as isotactic polypropylene and polytetrafluoroethylene [25,26]. Swelling of the "solids" portion of polyurethane aqueous dispersions by acetone solvent was non-destructively examined with TD-NMR in the past [27]. There are related examples in which the segmental mobility of hard segments in thermoplastic PU was studied with solid-state $T_{1\rho}$ relaxometry [28,29]. Applications are known using thermoplastic elastomers [30], including polyurethanes [31]. Oka et al.

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investigated conventional polyurethane foams, where it was found that the hard domain decreases in size as the water level in the foam formulation is increased [32]. The Bruker Minispec has been used by Mauri et al. to study the utility of TD-NMR in forensic analysis of resilient flexible foams with successful discrimination of many samples based on mapping on a segmental mobility vs. proton content coordinate system [33]. Sonnenschein et al. investigated high resiliency polyurethane foams with solid state NMR, where it was determined that the polyether soft segments have a mobile phase (soft domain) and a restricted mobility phase that was inferred to be at the interface of the hard and soft segment [34]. The ability to deconvolute signals that arise from components/domains is significant, since systems in which the phases have similar composition or density are generally difficult to characterize, such as is the case for poorly phase separated systems such as Visco foams. It is well known that the hard segments and soft segments have different glass transition temperatures (T_g) so their relative segmental mobility is different. By utilizing TD-NMR, relative segmental mobility of the various phase domains is characterized. The rapid detection via TD-NMR of the two-phase morphology particularly in the Visco foam series (relative to the detection via AFM) is discussed.

2. Materials and experimental methods

2.1. Materials

Details of the chemicals used are presented in Table 1. Polyol C is often used as a cell opener, due to its high functionality and molecular weight which builds up viscosity. The formulations of the resulting foam and blow off times are shown in Table 2. The main difference between the Flex (A) and Visco (B) foam series is the polyol equivalent weight — the Flex series uses a polyol with much longer polyether chain, which leads to sub-zero T_g and a very elastic foam. The Visco series uses a polyol with shorter polyether chain, leading to T_g that is closer to ambient temperatures. Water level is the only formulation variable for each series (Flex and Visco). Many studies exist where water level was varied in the formulation [35—39].

Isocyanate index ("ISO INDEX") refers to the stoichiometric ratio of isocyanate functional group to alcohol functional group (water counts as two alcohol groups) in the formulation. These are the same foam series as was reported in a previous publication by Aou et al. [40].

In addition, the A-series of foams have the following formulation: 100 parts per hundred polyol (pphp) of Polyol A, 0.18 pphp of

Table 1
Chemicals used in this study.

Chemical	Equivalent weight (g mol^{-1})	Functionality	Comments
Polyol A	1168	3	Poly(propylene-co-ethylene) oxide polyol
Polyol B	336	3	Polypropylene oxide polyol
Polyol C	1795	6.9	Multifunctional Poly(propylene-co-ethylene) oxide polyol
TDI	87.1	2	80:20 mixture of 2,4- and 2,6-toluene diisocyanate
SO	n/a	n/a	KOSMOS 29 Stannous octoate from Evonik
Amine A	n/a	n/a	DABCO 8264 from Air Products
Amine B	n/a	n/a	DABCO 33-LV from Air Products
Amine C	n/a	n/a	DABCO BL-11 from Air Products
Surfactant A	n/a	n/a	NIAX L-620 from Air Products
Surfactant B	n/a	n/a	NIAX L-627 from Air Products

Table 2
Foam formulations in this study.

Code	Type	Water (pph)	Blow off time (s)
A6	Flex	2.5	174
A7	Flex	3.8	116
A8	Flex	5.0	96
A9	Flex	6.3	99
B1	Visco	2.5	97
B2	Visco	2.0	115
B3	Visco	1.5	146
B4	Visco	1.1	157
B5	Visco	0.75	182

SO, 0.15 pphp of Amine A, 0.6 pphp of Surfactant A, and an ISO INDEX of 1.08.

The B-series of foams have the following formulation: 95 pphp of Polyol B, 5 pphp of Polyol C, 0.03 pphp of SO, 0.35 pphp of Amine B, 0.15 pphp of Amine C, 1.0 pphp of Surfactant B, and an ISO INDEX of 0.90.

2.2. Foam preparation

The samples in this study were made by box foaming under a fume hood using a $38 \times 38 \times 24$ cm ($15'' \times 15'' \times 9.5''$) wooden box lined with clear plastic film lining. A 16-pin (4 pins each in four radial directions that are separated by $90°$) mixer at high rotation speed was used at high rotation speed was used, together with a 1 gallon cup (16.5 cm diameter, 18 cm tall). The components in the formulation, with the exception of the SO and TDI, were mixed first for 15 s at 2400 rpm. Then the SO catalyst was added and immediately mixed for another 15 s at 2400 rpm. Finally TDI was added to the mixture and immediately mixed for another 3 s at 3000 rpm. Then the entire mixture is poured into the box lined with plastic film. The blow off time was measured from the moment the third and final mixing step starts, until the time when large numbers of bubbles appear at the top of the foam, which takes place after the foam reaches maximum height. Once foaming is complete, the foam is further allowed to cure overnight under the fume hood. Foam sample walls (2.5 cm) are discarded, and the remaining samples are characterized.

2.3. Atomic force microscopy (AFM)

A 1.0 mm $\times$ 0.5 mm $\times$ 5 mm piece was cut from the bulk with a razor blade, embedded in epoxy resin (Epo-Fix Embedding Epoxy; supplied by Electron Microscopy Sciences), and cured in a 40 °C oven for 24 h. The epoxy block was microtomed under cryogenic conditions (between -120 and -140 °C) to produce sections approximately 140—160 nm thick. The sections were placed on freshly cleaved mica and allowed to increase to room temperature under ambient conditions. Diamond knife was used for microtoming. The specimens were scanned with a Digital Instruments NanoScope IV, MultiMode AFM in Tapping Mode with phase detection. Software version is 5.30.3sr3. Nano-sensor tips were used in all experiments. The parameters of the tip: length of the cantilever $L = 235$ μm, tip radius $R < 10$ nm, Spring constant $k = {\sim}55$ N/m, cantilever resonant frequency $F_o \approx 160$ kHz. Tapping ratio $= 0.80$. Tuning voltage was set to 0.5 V. Unless otherwise noted, the AFM images shown are all phase contrast images.

2.4. Fourier-transform infrared spectroscopy (FT-IR)

Attenuated total reflectance-infrared spectra were acquired using the Nicolet NEXUS 670 Fourier-transform infrared spectrometer. A spectral resolution of 4 cm^{-1} was maintained, and 16 scans were co-added for acceptable signal-to-noise ratio. A Nicolet