

Probing Nanostructures of Biorenewable Polyurethane Collapsed Foams

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Abstract

Petroleum-based materials comprise the dominant resource going into the manufacturing of flexible foams. The rising cost of petroleum is providing the opportunity to implement vegetable-based resources into this expanding industry. 100% vegetable-based polyurethane (PU) flexible foams have been developed to exhibit viscoelastic properties comparable to their petroleum ether analogues.

Four vegetable-based collapsed foam samples were prepared and their glass transitions, mechanical moduli, and phase morphologies were studied. Glass transition temperatures and moduli were analyzed via differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Polyurea hard domain spacings were measured and visualized using small/wide angle x-ray scattering (SWAXS) and tapping mode atomic force microscopy (AFM). It was found that the soft domain glass transition temperature decreases as the molecular weight of the polyol structure increases.

Introduction

The chemical structure inherent to the vegetable oils varies in the degree and location of unsaturation, and determines the overall length of the fatty acid chains. By extending the polyol chain at the unsaturation points, the overall chain length increases. The goal of this experiment is to examine the effects of fatty acid chain length (i.e. polyol molecular weight) to thermal properties and phase morphology of PU foam.

During foaming, two competing reactions give rise to the phase separation of hard and soft domains. The gelling reaction is the polymerization of polyol with isocyanate to form the polyurethane soft segment (SS). The blowing reaction is the polymerization of isocyanate and water to form polyurea hard segments (HS). The hard segments eventually agglomerate during the reaction to form phase-separated hard domains throughout the continuous soft phase.

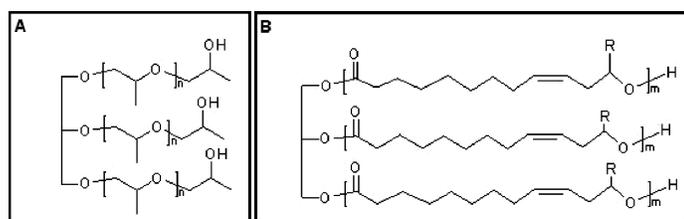


Figure 1: A) Petroleum polyether polyol. B) Vegetable-based polyol.

Experimental

Materials

The vegetable-based polyols used for this experiment were 1K, 2K, 3K, and 4K molecular weight polycondensate triols, Figure 1. These materials were polymerized using trimethylol propane (TMP) starter and ricinoleic acid via esterification synthesis. Arcol F3022 (Bayer Corporation), a petroleum polyether polyol that is comparable to the 3K polyol, Figure 1, was also used. An 80/20 mixture of 2,4 and 2,6-toluene diisocyanate (TDI) was stoichiometrically balanced to completely react with the water and polyols. The blowing catalyst used to accelerate the blowing reaction was DABCO®BL-11 (Air Products).

Procedure

All samples were made into collapsed foams (CF). Polyol, water, and catalyst were added to a 50 mL plastic beaker. TDI was added last and hand mixed for 10-20 minutes in a silicon oil heat bath at 55°C until the blowing reaction was complete, and the mixture was highly viscous or crumbling. The foam was poured into a 1.5 mm thick steel mold with 25 mm diameter circular cutouts. The mold was sandwiched between a layer of Teflon® followed by a steel plate. The plates were placed in a hydraulic press (Carver, Auto Series, model 3895) at 100°C and 15000 lbs. force for 1.5 h.

Characterization

Differential Scanning Calorimetry: DSC (Q1000, TA Instruments) was used to observe the SS glass transition temperatures. About 6-10 mg of the CF was placed and sealed into an Al hermetic pan. Heat flow data was taken over a temperature range from -100°C to 200°C at a rate of $10^{\circ}\text{C}/\text{min}$.

Dynamic Mechanical Analysis: DMA (ARES II, TA Instruments) measured the elastic modulus, G' , and loss modulus, G'' , over the temperature range of -100°C to 200°C . CF samples were cut to 12.65 mm width and placed in a rectangular torsion apparatus. A strain of 0.05% was applied and data was taken at a frequency of 3 rad/s.

Small/ Wide Angle X-Ray Scattering: SAXSess instrument (Anton Paar), operated at 12 kW and 50 mA, was used to determine hard domain spacings in samples. CF samples were cut and placed in a Cu sample holder and exposed to the x-ray source for 10 min. Scattering profiles were normalized to sample thickness.

Atomic Force Microscopy: An atomic force microscope (AFM) (Nanoscope III Multimode, Digital Instrument) was mounted on an optical microscope (Nikon). Tapping mode images were taken using a Si cantilever with a tip radius of about 100\AA and an oscillating resonant frequency of $\sim 240\text{ kHz}$. All images were taken under ambient conditions. Tapping oscillations were conducted in the repulsive regime and with resolution of 512×512 pixels.

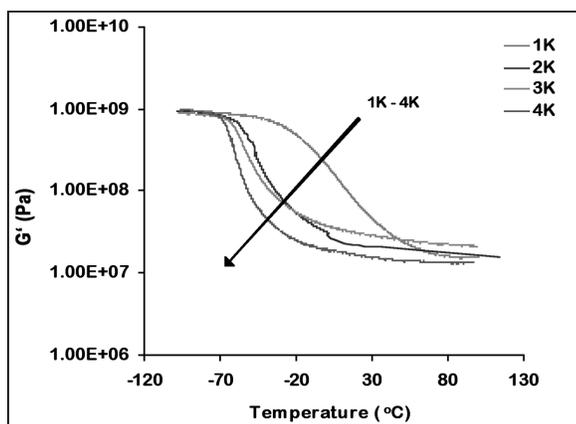


Figure 2: Dynamic mechanical analysis.

Results and Discussion

With increasing the weight of the vegetable oil structure, the PU foam's T_g decrease as seen in Figure 2. The initial drop in G' data around -60°C corresponds to the increase in SS mobility. The temperature is the T_g of the soft domains. SAXS, Figure 3, gives an average value of hard domain spacings; a characteristic shared with the petroleum analogues. AFM provides a localized map of the phase morphology. A 500 nm phase image of 4K MW polyol is shown in Figure 4. Hard domains are brighter regions, and

soft domains are darker regions. The phase scale was adjusted to show a clear contrast between the two regions. The hard domains agglomerated into tiny sphere-like orbs and distributed in the SS matrix. All images were plane-fitted to remove large scale surface curvature for better height profile displays. From experimental results, biorenewable polyols can potentially replace petroleum feedstock, making a novel substitute in industrial production of PU flexible foams. Thermal properties, such as T_g , of vegetable based PU can be tuned via the control of polyol MW.

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References

- [1] Zhang et al. Comparison of Polyurethane Flexible Foams: Polyether vs. Soybean Oil-based Polyols. Submitted for Pub.

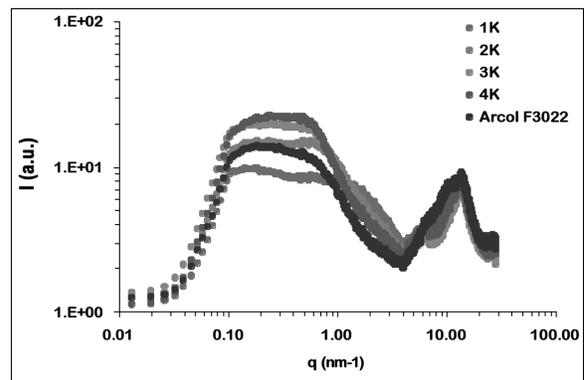


Figure 3: Small/wide angle x-ray scattering.

Figure 4: Atomic force microscopy image.

