Synthesis, Characterization and Modeling of Urethane Networks.

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1. Abstract

Elastomeric networks of polyurethane common to the sole-shoe industry were obtained and characterized to study the relationship between network structure and rheological properties. A bi-functional polyol spacer was used to dilute the crosslinking agent so networks of different crosslinking density were synthesized. Structural parameters were obtained with swelling and sol-gel techniques along with dynamic mechanical analysis rheometry. Efforts to model the network structure include the use of the Macosko-Miller recursive method as well as the ideal rubber model. Acceptable agreement of the dynamic elastic modulus with the ideal rubber model is obtained at low crosslinking densities. Further work is necessary to include the behavior of networks at high crosslinking densities.

2. Introduction

Polyurethane (PU) is a versatile material that can be used as laminates, adhesives, foams, paints, coatings and three-dimensional diverse materials. PU properties can be controlled by an appropriated selection of its precursor materials: isocyanates and polyols. The resulting properties are in the middle point of typical rubbers and plastics. Interesting properties are related to the bioengineering sciences [1-4] because they are biocompatible materials with hemocompatibility [5] properties. The surgical implants industry and the specialty needs shoe industry find in PU good candidates for the treatment of prosthesis [6] in diabetic patient management and control. Soft tissue [7] and dental [8] applications of PU are well studied. Most of these applications of PU are based on crosslinked materials, hence the need to have model networks studies to relate structure to properties into a coherent model.

3. Experimental

3.1 Synthesis

Urethane model networks (UMN) were prepared from a polydiol (Dow Chemical P-852, 2040 g/eq), butanediol (Aldrich), a diisocyanate prepolymer (diphenylmethyldiisocyanate, MDI, 442 meq/g) and a polytriol (Dow Chemical P-505, 1851 g/eq) used as crosslinking agent, catalyzed by a mixture of dibutyl tin dilaurate (DBTDL) and a tertiary amine 1,4-diazobicyclo[2,2,2]octane (DABCO). The synthesis was done in a stirred batch reactor until gel onset was detected afterwards, the polymerization concluded by compression molding.

3.2 Characterization

UMN were characterized by FT-IR (Nicolet 510, KBr pellets), solubility tests (tetrahydrofurane, chloroform, dimethylformamide, ethylacetate, dichloroethane, cholobencene, glycerol, toluene, acetone, water), sol-gel measurements, swelling kinetics,, DSC (Perkin-Elmer DSC-7, nitrogen carrier, 40 to 250 degC, ramp 10 degC/min), TGA(Shimadzu TGA-40, nitrogen carrier, room temp to 700 degC, ramp 20 degC/min), DMA (Rheometrics RDS-II, rectangular torsion bar, room temperature, 1% deformation, frequencies 1, 10, & 100 rad/s)

3.3 Modeling

Crosslinking density of UMN was calculated with the Recursive Method of Macosko and Miller [9, 10], predicting the elastic moduli was done following the Ideal Rubber Theory following Macosko's approach [11].

4. Results and Discussion

Figure 1 shows results for the urethane networks as a function of the amount of crosslinker. Properties such us (a) apparent density and (b) elastic modulus (G')

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(a) **(b)** **(c)**

Figure 1.: *Urethane networks characterization as function of the crosslinker level* ***(a)*** *apparent density,* ***(b)*** *frequency dependence of the elastic moduli.* ***(c)*** *prediction of the elastic moduli.*

Structural parameters (Table 1) were obtained with swelling and sol-gel techniques along with dynamic mechanical analysis rheometry. The efforts to model the network structure included the use of the Macosko-Miller recursive method as well as the ideal rubber model are shown in Figure 1(c).

Table 1 *Recursive Method parameters for model urethane networks calculated from network characterization techniques*

Model Network	Crosslinker level (%)	Sol fraction	Crosslinking density (mol / L)
PU-E1	84.8	0.024	0.075
PU-E2	64.1	0.025	0.066
PU-E3	50.8	0.029	0.038
PU-E4	40.4	0.030	0.027
PU-E5	27.1	0.034	0.020

5. Conclusions

Acceptable agreement of the dynamic elastic modulus with the ideal rubber model is obtained at low crosslinking densities. Further work is necessary to include the behavior of networks at high crosslinking densities.

6. References

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