Chemical Recycling of Rigid and Flexible Polyurethane as Raw Materials

Dai Soo Lee

Division of Environmental and Chemical Engineering, Chonbuk National University, Jeonju 561-756, Korea

Introduction

Polyurethane is one of versatile polymers for foams, elastomers, fibers, and adhesives. Various types of polyurethane wastes are generated in industries and the amount of wastes to be treated amounts to 20,000 tons every year in Korea. In spite of the large amounts of the wastes, most of them are being incinerated. Incineration of polyurethane wastes has problems of air pollution and corrosion of facilities. Most of polyurethane wastes are thermosets. Thus, physical recycling of polyurethane is very limited to pulverization into powder to be used as fillers. On the other hand, in chemical recycling of polyurethane via depolymerization of polyurethanes with glycols or amines, we can get valuable chemicals useful for various applications.

Depolymerization of rigid polyurethanes with glycols results in mixtures of glycols and amines. Amines in the depolymerization products make the products so reactive as raw materials of polyurethanes. Thus, deamination of glycolysis products of polyurethanes are necessary. Depolymerization of flexible polyurethanes results in phase separated products of amine rich phase and polyol rich phase. Separation process for the depolymerized products are required. It is expected that depolymerization of flexible polyurethanes with caprolactam results in homogeneous products due to condensation and exchange reaction of aminocaproic acids during the chemical recycling process. For the homogeneous products, there is no needs to develop a process to separate amine rich phase and polyol rich phase in the depolymerization products. Highlights of our studies on the chemical recycling of polyurethanes with caprolactam are reported in this paper.

Experimental

Depolymerization of Spandex Scraps Spandex scraps containing 50wt% of dimethyl formamide as solvents and caprolactam dissolved in water were introduced into 1 L reactor at room temperature in dry nitrogen gas environment. Ratios of spandex and caprolactam were varied from 100/20 to 100/50 by wt. Mixtures were heated to 200℃ and depolymerization were carried out for 8 hours. Table 1 gives sample codes, composition of depolymerization systems, and hydroxyl values of the products obtained.

Table 1. History of PSK

Sample Code	Composition (by wt)	Hydroxyl values(mgKOH/g)
CPL-20	Spandex/CPL=100/20	52
CPL-30	Spandex/CPL=100/30	49
CPL-40	Spandex/CPL=100/40	45
CPL-50	Spandex/CPL=100/50	43

Preparation and Evaluation of Polyurethane Elastomers To prepare polyurethane elastomers with depolymerzation products, stoichiometric amount of polymeric 4,4-diphenyl methane diisocyanate (MDI) from Kumho Mitsui, PM 27, were mixed with the depolymerization products by mechanical mixer and cast into silicone mold to make specimens for the characterization. Mixtures of depolymerization products and polymeric MDI were cured in oven at 100℃ for one day. Differential scanning calorimeter (DSC) and dynamic mechanical analyzer (DMA) were employed to study thermal properties of polyurethane elastomers. A universal testing machine was also used to get stress-strain properties in tensile mode following ASTM D 256.

Results and discussion

Thermal properties Figure 1 shows DSC thermograms of polyurethanes prepared from CPL-20 and PM 27. Polyurethanes based on CPL-30, CPL-40, and CPL-50 showed similar thermograms. Soft segment glass transition temperatures of polyurethanes (Tg) were

observed around at -70℃ and the Tg increased with isocyanate index. Exotherms and endotherms due to crystallization and melting of poly(tetramethylene ether glycol) which was used in the preparation of Spandex were observed in -30~40℃. We found that the soft segment Tgs were little affected by the recipe of depolymerization even though hydroxyl values of the depolymerization products were dependant on the recipe in Table 1. Results of dynamic mechanical analyses are not given in this article because of limited space. In dynamic mechanical analyses, we could confirm similar characteristics observed in Figure 1. It is speculated that the microphase separation of the polyurethane elastomers investigated are hardly affected by the depolymerization recipe.

Physical properties of polyurethane elastomers depend on hard segment contents and microphase separation of hard segments. Hard segments of polyurethane elastomers were increased by adding additional short chain diol, ethylene glycol to the depolymerization products. Figure 2 shows stress-strain curves of polyurethane elasomers prepared with additional ethylene glycol, CPL-20, and PM-27. It is observed that tensile modulus, the initial slope of stress-strain curve, and tensile strength increase with increasing the content of ethylene glycol. The increase of tensile modulus and tensile strength is attributable to the increase of hard segment contents of the polyurethane elastomers. We found that the elasotomers show acceptable tensile properties for various applications such as polyurethane binders.

Conclusion

As a part of studies on chemical recycling of polyurethane, Spandex fiber scraps were depolymerized with caprolactam and homogeneous products were obtained. We could prepare polyurethane elastomers with the depolymerization products, polymeric MDI, and additional ethylene glycol to control hard segment contents of polyurethane. Thermal and mechanical properties of the polyurethane elastomers were acceptable for various applications.
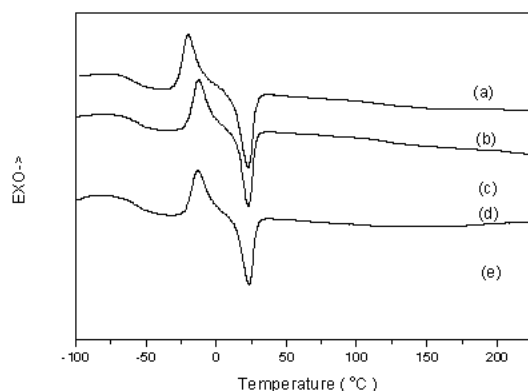

Figure 1 . DSC thermograms of PU elastomers prepared from CPL-20 in different iso index : (a) 95; (b) 100; (c) 105; (d) 110; (e) 115.
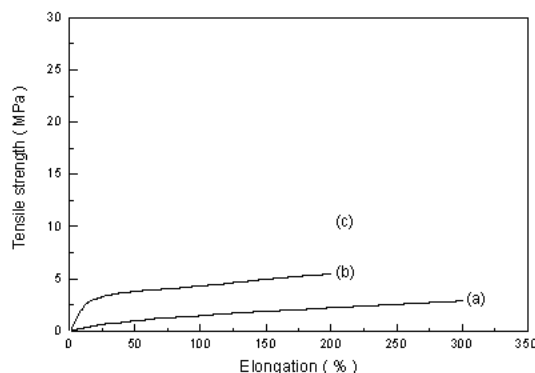

Figure 2. Stress-strain curves of PU elastomers based on CPL-20 with additional chain extender (moles of EG): (a)1 ; (b) 2 ;(c) 3.