Biodegradable Polyurethane Materials from Bark and Starch. I. Highly Resilient Foams

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ABSTRACT: Liquefaction of the bark of *Acacia mearnsii* (BK) and cornstarch (CS) was conducted by using a solvent mixture consisting of poly(propylene glycol) (PPG), glycerol, and sulfuric acid with a weight fraction of 94/5/1 at 150°C. Solubilities of BK and CS were about 80% after 60 min and 100% after 20 min in the same solvent, respectively. Highly elastic or highly resilient (HR) polyurethane foams (PUFs) suitable for car-seat cushions were prepared from the liquefied BK and CS without removing the insoluble residue from the liquefaction mixture. About 20% of the insoluble residue from BK contributed remarkably to the improvement of flame resistance of the resulting PUFs. HR PUFs having better resilience properties were prepared using PPG of molecular weight around 4000, as compared with poly(ethylene glycol) having the same hydroxyl value. PUFs were synthesized from three BKs with different tannin contents, that is, BK0 (tannin: 0%), BK1 (tannin: 43%), and BK2 (tannin: 48.5%), to evaluate the effect of the tannin content on their performance of resilience. Both the resilience value and density of the PUFs increased with increasing BK content for all BK systems. BK2 was chosen to prepare PUFs in the further work. When CS replaced part of BK, the density and compressive strength of the PUFs decreased with an increasing cornstarch proportion, whereas the resilience value had its maximum value when the weight ratio of CS:BK was 1:1. The PUFs were, to some extent, biodegradable: The average weight loss of samples buried in soil for 6 months was 15.6 wt %. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2575–2580, 2000

Key words: bark; starch; polyurethane foams; biodegradability

INTRODUCTION

Polyurethane foams (PUFs) are used widely in many fields as structural, cushion, insulation, electrical, flotation, and packaging materials. Much attention is paid to introducing plant resources into PUF production. The materials prepared from biomass not only open a new and efficient way to use regeneratable natural resources, but also possess a great potential for bio- and photodegradability. The latter advantage is more striking in the urgent need of environmental protection.[1] Natural polymers containing more than one hydroxyl group in the main chain are expected to be utilized as polyols for polyurethane preparation.[2–5] We prepared PUFs with moderate strengths and biodegradabilities from wattle tannin (WT) or the bark of *Acacia mearnsii* (BK) and diisocyanate in the presence of synthe-

sized polyester.[6,7] It was proved through careful studies on a model reaction[8] that WT, which is the main component of BK, can act as a crosslinking agent in polyurethane molecules and it will improve the compressive properties of PUFs.[6,7] However, the density of tannin PUF was higher than those of the commercially produced PUFs; this may lead to higher production costs. Recently, Nakashima et al.[9] prepared low-density rigid PUFs from polyol mixtures of barks of *A. mearnsii* or *Cryptomeria japonica* with poly(ethylene glycol) (PEG) 400. Yao et al.[10] reported the method to prepare PUFs from combined liquefaction of wood and starch in a PEG400/glycerol-blended solvent using sulfuric acid as a catalyst.[10] But those methods are not suitable for the preparation of flexible PUFs, because, in that case, polyol with a larger molecular weight is indispensable.

Flexible PUFs for car cushions need a high crosslinking density to supply a high-resilient property. Components with benzene rings and a flexible configuration such as diethanolamine are usually introduced into the PUF formulation as crosslinking agents to improve the compressive strength and resilience.[11]

In this study, a new kind of effective, environmentally safe, and low-cost crosslinking agent—BK—was introduced into the preparation of high-resilient flexible PUFs. The liquefaction of bark in a solvent mixture consisting of larger molecular weight poly(ether polyol) and glycerol with sulfuric acid as a catalyst was investigated. The effects of the preparation conditions on properties needed for cushion material are discussed.

EXPERIMENTAL

Materials

BK (*A. mearnssi* De Wild: 80 mesh pass) and cornstarch were dried in an oven at 105°C for 24 h before use. Poly(propylene glycol) (PPG; GEP-330N, hydroxyl value 35 mg KOH/g; viscosity: 800–1000 cp/25°C) was kindly supplied by the No. 3 Chemical Plant of Shanghai GAO QIAO Petrochemical Co. (Shanghai, China). Other chemicals used were reagent grade and obtained from commercial sources.

Liquefaction Solvent and Procedure

Liquefaction was conducted using the acid catalyst method similar to the procedure given by Yao

et al.,[10] using a liquefaction solvent mixture consisting of PPG, glycerol, and a sulfuric acid catalyst with a weight fraction of 94/5/1. The solvent and the catalyst (100 g in total) were premixed thoroughly in a three-necked flask equipped with a mechanical stirrer and a nitrogen inlet. Then, the BK powder was introduced in the flask and the temperature was increased to 150°C within 30 min. The liquefaction mixture was maintained at this temperature with stirring and refluxing under a nitrogen atmosphere for 30 min and followed by adding a predetermined amount of the cornstarch as a second biomass component at this temperature for another 20 min if needed. After that, the flask was cooled to room temperature and the excessive sulfuric acid was neutralized with an equivalent amount of a sodium hydroxide aqueous solution (48 wt %). The hydroxyl value of a liquefaction mixture was determined by the method described by Yao et al.[10]

Determination of the Liquefaction Extent of the Biomass

The liquefaction extent of the biomass was determined after a prescript liquefaction time by the dioxane/water binary diluent method described by Yao et al.,[1] that is, the liquefied mixture was diluted by an adequate amount of dioxane/water (8/2), stirred in a magnetic stirrer for more than 4 h, and then vacuum-filtrated through a Q/XHJ3017 filter paper. The residue was rinsed by the diluent repeatedly until a colorless filtrate was obtained, and then the residue was dried to a constant weight. The residue content of the biomass was calculated by the following equation:

Residue content

$$= (1\text{weight of residue/weight of total biomass})$$
$$\times 100\%$$

Preparation and Characterization of PUF Foam

The definite amounts of biomass polyol, catalyst, surfactant, water, and other additives, if any, were premixed thoroughly in a paper cup with a mechanical stirrer. To this mixture, a calculated amount of tolylene diisocyanate (TDI) was added to give an isocyanate index of 110 and stirred at 2400 rpm for 10–15 s. The mixture was then poured immediately into a 12 × 12 × 10-cm mold and was allowed to increase at room temperature. The resulting foam was removed from the mold

after 1 h and was allowed to cure at room temperature for 1 week before cutting into test specimens. The ball rebound resilience value, flammability, and compressive strength of the PUFs were measured according to ASTM D 3574-81, GB 8410-94, and the method described in a previous report,[6] respectively.

The isocyanate index is defined as follows:

$$\text{Isocyanate index} = [M_{\text{TDI}} \times W_{\text{TDI}}/(M_{\text{LD}} \times W_{\text{LD}}$$
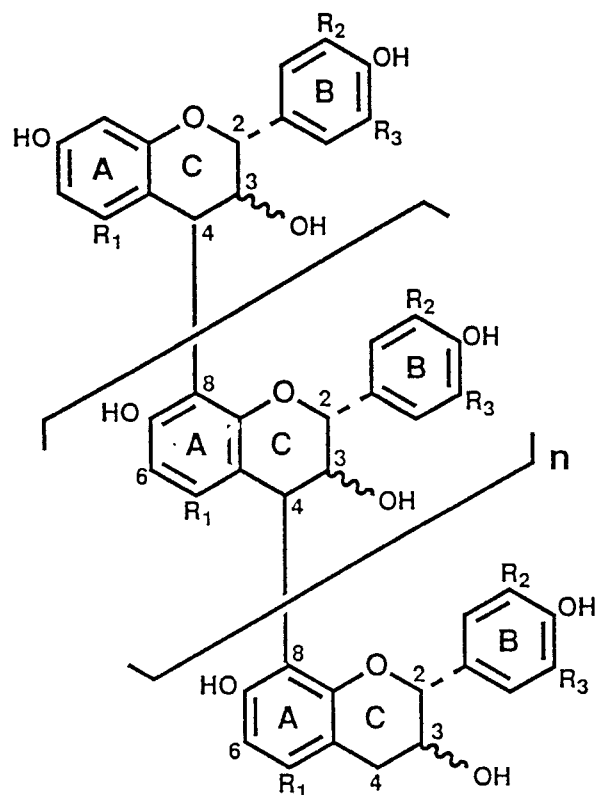$$+ \, 2/18 \times W_W)] \times 100$$

where M_{TDI} is the isocyanate group contents in TDI (mol/g); W_{TDI}, the weight of TDI (g); M_{LD}, the hydroxyl group content in liquefied biomass (mol/g); W_{LD}, the weight of liquefied biomass (g); and W_W, the weight of water in the foam formulation (g).

RESULTS AND DISCUSSION

Effect of Liquefaction Solvent Composition

PUF prepared from a poly(ether polyol) such as PPG or PEG has comparatively low density and high resilience because of the low viscosity of the polyether prepolymer and the low rotation hindrance of ether bonds in the main chain. However, the high chain flexibility also led to low compressive strength. Usually, two methods are used to improve the compressive strength: first, introducing an aromatic group to the main chain to improve the chain rigidity; and, second, increasing the use level of the crosslinking agent such as diethanolamine and trimethylol propane to increase the crosslinking density of the polymer chain.[11] In our previous works, we reported that tannin and tannin-containing BK could act as effective crosslinking agents in the preparing of PUFs.[6,7] In this article, it is expected that the tannin component in BK can improve both the strength and resilience of PUFs because tannin has not only phenyl groups for the improvement of chain rigidity and ether bonds for the changing of chain configuration but also enough active hydroxyl groups for crosslinking as shown in Figure 1.

BK should be liquefied in larger molecular weight polyols so as to produce flexible PUFs. Two kinds of poly(ether polyol), PEG and PPG having the same hydroxyl value of 35 mg KOH/g, were used for preparing PUFs from BK. The PUFs

R₁=H, R₂=H, R₃=H ---- Progibourtinidin
R₁=H, R₂=OH, R₃=H ---- Profisetinidin
R₁=H, R₂=OH, R₃=OH ---- Prorobinetinidin
R₁=OH, R₂=H, R₃=H ---- Propelargonidin
R₁=OH, R₂=OH, R₃=H ---- Procyanidin
R₁=OH, R₂=OH, R₃=OH ----Prodelphinidin

Figure 1   Structural diagram of taninn.

from PPG gave higher resilience values than those from PEG at given BK contents (Fig. 2). On the other hand, solubilities of BK were about 85, 80, and 50% in PPG with the number-average molecular weights (M_n) of 3000, 4000, and 5000, respectively. However, the resilience values of PUF showed a maximum value at an M_n of 4000 as shown in Figure 3. Thus, polyether PPG GEP-330N with an M_n of 4000 and viscosity of 800 cP was selected to prepare highly resilient (HR) PUFs in the further work.

Effect of Tannin Content in Bark on Resilient Value and Density of PUFs

To evaluate the effect of the tannin content on the resilience of PUFs, we synthesized PUFs from three BKs with different tannin contents, that is,
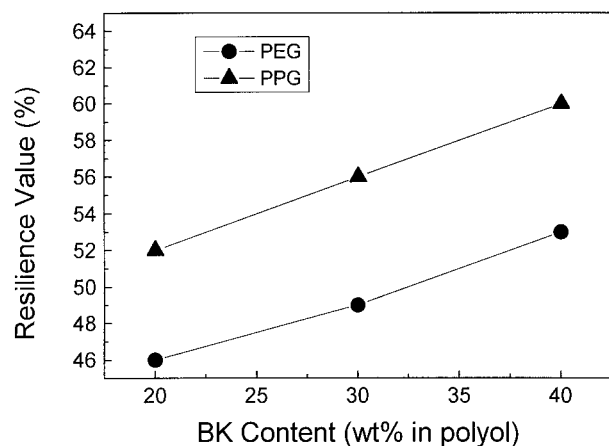
Figure 2 Effect of bark content in polyol on the resilience value of PUF: (△) PPG; (●) PEG. NCO/OH: 1.1; diethanolamine: 0.5%; DBTL: 0.32%; water: 0.4%; TEDA: 0.03%; silicon oil (Y10366): 2.0.

BK0 (tannin: 0%, residue after tannin extraction), BK1 (tannin: 43.0%), and BK2 (tannin: 48.5%); the results are shown in Figure 4. Both the resilience values and densities of the PUFs increased with increasing BK contents for all BK used. The densities of PUFs from BK2 were slightly larger than those of BK1 and BK0 at given tannin contents as shown in Figure 5. Since both the resilience value and the density are important properties of PUFs, the ratio of the resilience value/density (R/D) was calculated to evaluate their combined effect on the PUFs and the results are shown in Table I. The larger the R/D ratio, the better the PUF properties for car-cushion use.
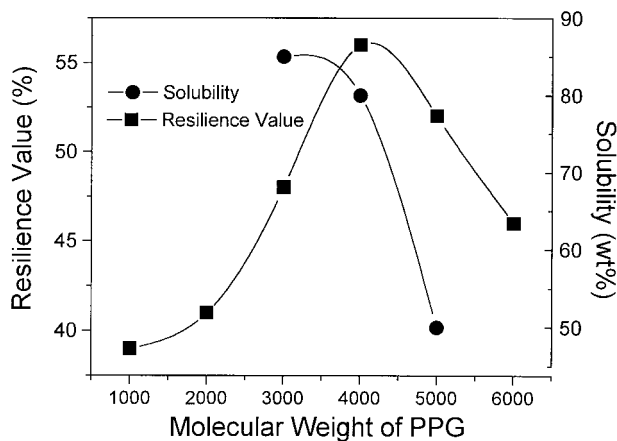

Figure 3 Effect of molecular weight of PPG on the solubility of bark and the resilience value of PUF. NCO/OH: 1.1; diethanolamine: 0.5%; DBTL: 0.32%; water: 0.4%; TEDA: 0.03%; silicon oil (Y10366): 2.0%.
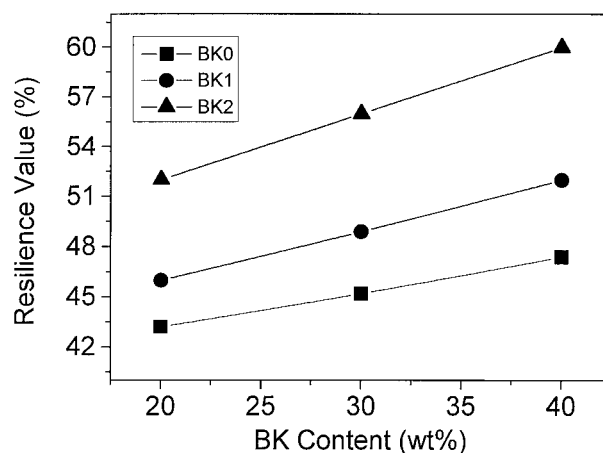

Figure 4 Effect of bark content on the resilience value of PUF: (□) BKS (tannin content = 0%); (○) BK1 (tannin content = 43.4%); (△) BK2 (tannin content = 48.5%). NCO/OH: 1.1; diethanolamine: 0.5%; DBTL: 0.32%; water: 0.4%; TEDA: 0.03% silicon oil (Y10366): 2.0%.

The R/D of PUFs from BK2 possessed the best values at a given BK content. This can be ascribed to the highest tannin content in BK2. BK2 was chosen for all the syntheses described hereinafter.

Effect of Cornstarch Content in Biomass on Resilience of PUFs

Cornstarch totally dissolves easily in a PEG400/glycerol mixture,[1] and there are many glycoside bonds in its main chain that may contribute to the
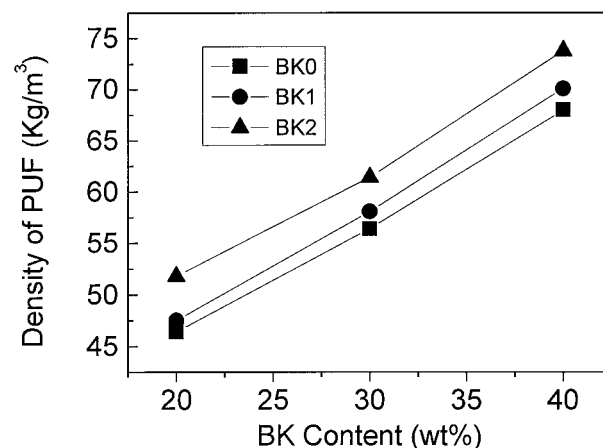

Figure 5 Effect of bark content on density of PUF: (□) BKS (tannin content = 0); (○) BK1 (tannin content = 43.4%); (△) BK 2 (tannin content = 48.5%). NCO/OH: 1.1; diethanolamine: 0.5%; DBTL: 0.32%; water: 0.4%; TEDA: 0.03%; silicon oil (Y10366): 2.0%.

Table I   R/D Value of PUFs Derived from BK2, BK1, and BK0

BK Content (%)	20	30	40
BK2	1.1	0.91	0.81
BK1	0.97	0.84	0.74
BK0	0.93	0.80	0.69

resilience of PUF, so we tried to use CS as the second biomass component. It can be totally dissolved in the liquefaction mixture within 20 min at 150°C. From Figures 6 and 7, it can be seen that when CS replaced a part of BK the density and compressive strength of the PUFs decreased with an increasing CS proportion, whereas the resilience value showed a maximum at CS/(CS + BK) value of 50%, that is, 1:1 of CS:BK.

Effect of Insoluble Bark Residue on Flammability of PUFs

Flame resistance is an important property from a burning safety point of view. We found that the flame resistance of the PUFs derived from BK is remarkably better than that of PUFs without BK. More interestingly, the insoluble BK residue plays an important role in the flame-resistance properties of BK-derived PUFs. The insoluble residue removed from a liquefaction mixture of BK was partly added back to the liquefaction mixture containing no insoluble residue; then, PUFs were prepared from the mixture. The flammability was plotted against the insoluble residue contents in the liquefaction mixture as shown in Figure 8. It
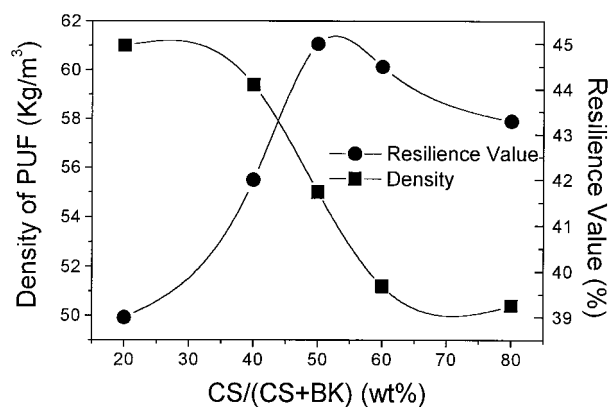

Figure 7   Effect of cornstarch content in total biomass on compressive strength of PUFs. NCO/OH: 1.1; diethanolamine: 0.5%; DBTL: 0.32%; water: 0.4%; TEDA: 0.03%; silicon oil (Y10366): 2.0%.

can be seen that the flammability of PUFs decreased with the increasing insoluble residue in PUF. This improvement of flame resistance may be caused by the inorganic components in BK. A more detailed mechanism for this flame-resistance effect is under study and will be reported later.

Biodegradability

Three categories of PUFs, the first one containing 30% BK, the second one containing 15%BK and 15%CS, and the third one commercially pur-

Figure 6   Effect of cornstarch content in total biomass on resilient ratio and density of PUFs. NCO/OH: 1.1; diethanolamine: 0.5%; DBTL: 0.32%; water: 0.4%; TEDA: 0.03%; silicon oil (Y10366): 2.0%.
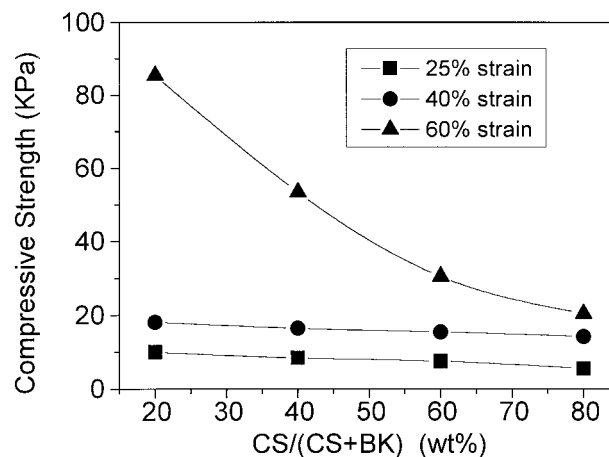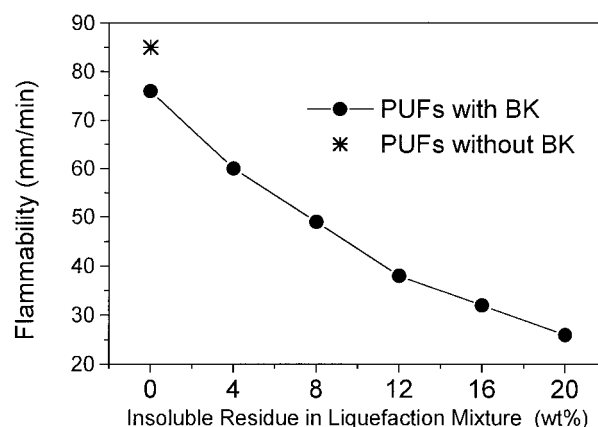

Figure 8   Effect of the amount of insoluble bark residue removed from liquefaction mixture on the flammability on PUF. NCO/OH: 1.1; diethanolamine: 0.5%; DBTL: 0.32%; water: 0.4%; TEDA: 0.03%; silicon oil (Y10366): 2.0%.
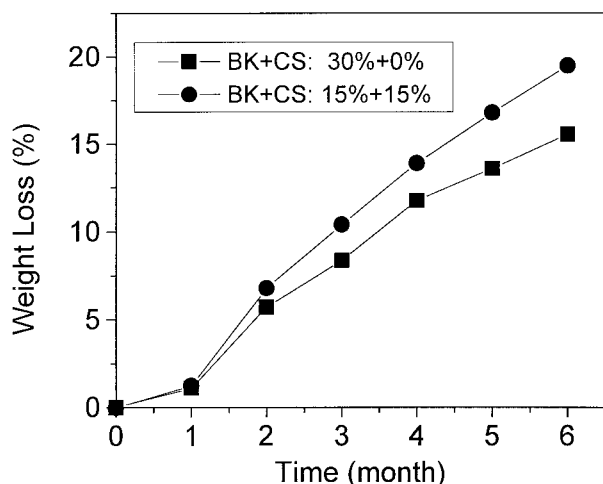
Figure 9 Effect of soil microorganisms treatment on weight-loss behavior of PUFs.

chased, were buried in soil. It can be seen from Figure 9 that the weight losses of two PUF samples derived from the biomass increased with increasing periods of soil-microbial treatments, and the PUFs containing BK and CS showed a slightly faster weight loss behavior than those containing the BK only. These results indicate that the CS component in PUFs are decomposed more easily by soil microorganisms than is the BK component. On the other hand, almost no change was observed in the weight of commercially obtained PUF (data not shown). The above-mentioned results indicate that the biomass component contributes mainly to the biodegradability of the PUFs.

CONCLUSIONS

Highly elastic or highly resilient polyurethane foams suitable for car-seat cushions can be prepared from liquefied BK and CS. Insoluble residue from BK liquefaction contributes remarkably to improvement of the flame resistance of the resulting PUFs. When CS replaced part of the BK, the density and compressive strength of the PUF decreased with increasing cornstarch proportion, whereas the resilience value has its maximum value when the weight ratio of CS:BK is 1:1. The PUFs were, to some extent, biodegradable; the average weight loss of the samples buried in soil for 6 months is 15.6 wt %.

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