# Synthesis and Characterization of Starch-Based Polyurethane Foams

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**ABSTRACT:** Starch-based polyurethane foams were synthesized by reacting a mixture of starch and polycaprolactone triol with an aliphatic diisocyanate, in the presence of water as blowing agent. Some foams were also prepared by adding a certain amount of polyethyleneglycol. The reaction kinetics is affected by the presence of starch due to the higher viscosity related to the presence of the high molecular weight polysaccharide. Starch-based polyurethanes show higher glass transition temperatures and lower thermal stability. Cellular materials with different mechanical properties can be obtained by varying the amount of starch and by controlling the relative amount of polycaprolactone triol and polyethyleneglycol in the composition. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 739–745, 1998

**Key words:** starch; polyurethane foams; kinetic; mechanical properties

## INTRODUCTION

Polyurethane (PU) foams can be assumed to be composite structures resulting by the controlled entrapment of gases that are generated during the polymerization reaction between polyfunctional alcohols and polyisocyanates to form urethane linkages. These foams exhibit—in comparison with other materials—physical and mechanical properties related to their chemical composition and density, particularly suitable for use in many applications (such as seating, cushioning, fabric insulation, and packaging).[1,2]

High volumes of PU foams are produced every year, and the disposal of these materials is becoming a serious problem. Government regulation in Europe and in the United States, regarding waste disposal, will result in a reduction of the use of landfills and an increase of the recycling and incineration of these materials. Unfortunately, due to the thermosetting characteristics of PUs, recycling is difficult and limited; therefore, biodegradation can be considered as a possible alternative for the solution of the waste problem generated by PUs.

Biodegradable polymers have found applications in medicine, such as sutures, wound dressings, surgical implants, controlled-release, and drug delivery systems where the higher costs of these materials is justified.[3] Biodegradable plastics are, however, suitable in many commodity applications, such as garbage bags, food and beverage containers, and packaging; but, their use is still limited due to their high cost or their low performances.[4] Modification of the physical and chemical properties of these materials, through reaction or blending with other biodegradable and nonbiodegradable polymers, is often necessary to meet the required performances.[5–7]

The synthesis of biodegradable PUs is a relatively recent issue in PU chemistry, and only a few works have been published compared with a

**Table I   Composition of the Reaction Medium for S/PCLt Foams**

| Ingredient | Parts Per 100 Parts Polyol (pphp) |
|---|---|
| S + PCLt + PEG | 100 |
| Water | 6.4 |
| Silicone oil | 1.9 |
| N,N-Dimethyl benzylamine | 0.3 |
| Dibutyltindilaurate | 0.8 |
| 1,6-Diisocyanatehexane | 118.8 |

higher number of recent patents. It is well known that polyester-based PUs are much more susceptible to biodegradation than PUs derived from polyether diols.[8] PUs obtained by reacting aliphatic and aromatic diisocyanates with poly(caprolactonediol)s of various molecular weights were treated with microorganisms and enzymes. In general, the more flexible the PUs, the more susceptible they are to biodegradation.[9] Poly(ester urethanes) were also synthesized by using biodegradable polyester segments, such as lactic acid,[10,11] poly(3-hydroxybutyrate),[12] and polyethylene adipate.[13]

A successful method of increasing biodegradability is to develop biopolymer-based materials.[14,15] Cellulose, starch, proteins, lignine, microbial polysaccharides, and microbial polyesters are naturally occurring polymers obtained from renewable sources. They are readily biodegradable and tend to degrade in biologically active environments like soil, sewage, and marine locations where bacteria are active.

Biodegradable PU composites have been synthesized using hydroxyl groups contained in plant material and/or fibers and molasses using MDI as diisocyanate.[16] Other biodegradable PU foams were prepared by neutralizing a reaction solution containing liquefied lignocellulosic substances (obtained by treating lignocelluloses with polyvalent alcohols in the presence of an acid catalyst), by primary and/or secondary amine—which may contain alkali and alkali earth metal hydroxides—and then treating with a polyisocyanate in the presence of a blowing agent.[17]

This article reports on the results of synthesis and characterization of starch-based PU foams. Starch, which is the second largest biomass produced on earth, has been widely used in blends with nonbiodegradable[18–20] and biodegradable[21,22]

polymers, either to lower the total cost and/or to improve the biodegradability of the material. The hydroxyl functionality of this biopolymer allows chemical reactions with conventional diisocyanates. However, the use of starch in the synthesis of PU foams has been reported in only a few publications.[23–26] In this work, a mixture of destructurized starch and low molecular weight polycaprolactone triol (PCLt) was used in the reaction with an aliphatic diisocyanates. The effects of starch content on polymerization kinetics, on the thermal and mechanical properties of foams, were studied.

## EXPERIMENTAL

### Materials

PU foams were prepared using soluble starch (S), PCLt ($M_w$ = 300), and 1,6-diisocyanatohexane (HDI). Silicone oil, dibutyltin dilaurate, and N,N-dimethylbenzylamine were used as surfactant and catalysts. All of the reagents were supplied by Aldrich Chemical Company (Milwaukee, WI).

Composition of the reaction medium is reported in Table I. Starch was added to the polyol mixture up to 40% (w/$w_{polyol}$). To investigate the effect of a flexible polyether on the thermal and mechanical properties, foams were also synthesized by using polyethyleneglycol (PEG) ($M_W$ = 200; Aldrich Chemical Company) in addition to polycaprolactone and starch.

Polyol(s) and starch were mixed into a Teflon
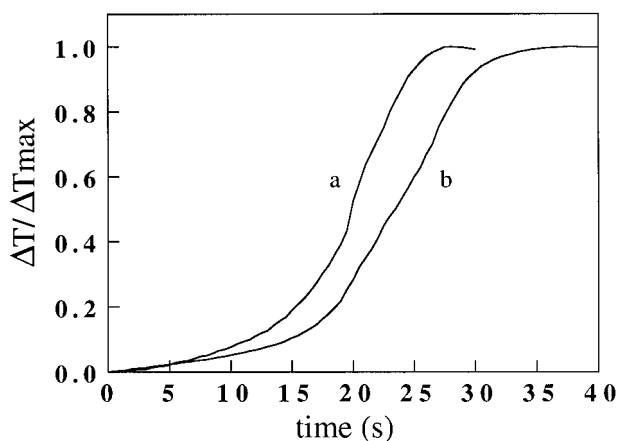


**Figure 1**   Effect of starch on the reaction kinetic. S/PCLT ratio: (a) 0/100 and (b) 30/70.
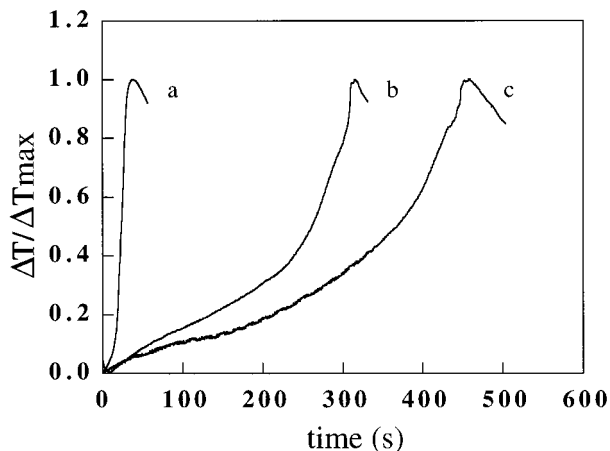
**Figure 2** Effect of dibutyltindilaurate on the reaction kinetic. The concentrations, expressed in parts of dibutylindilaurate per 100 parts of polyol are: (a) 0.8; (b) 0.6; and (c) 0.4.

beaker at 55°C and stirred for 5 min at 750 rpm before adding the silicone oil, water and the amine catalyst. HDI and dibutyltin dilaurate were added after 5 more minutes, and the mixture was stirred for few seconds up to the whitening of the liquid (cream time). Stirring was then stopped, and the mixture was quickly poured into a Teflon close-top container and preheated at 55°C. Foams were kept in an oven at 55°C for 1 h to permit the completion of the reaction and then stored at room temperature for 24 h before testing.

### Methods

#### Polymerization Kinetics

The reaction kinetic was followed by monitoring the temperature of the reaction medium before and during the foam formation through a thermocouple connected to a computerized data acquisition system.

#### Thermal Properties

Calorimetric analysis was performed by means of a Mettler TA 30. Samples were heated twice from −50°C to 120°C at a heating rate of 10°C/min.

Thermogravimetric analysis was performed with a TA Instrument, model 951 (Du Pont Instruments, New Castle, DE) from 20°C to 700°C either under nitrogen or air flux.

#### Mechanical Properties and Morphology

An Instron machine, model 4204, was used to investigate the mechanical properties of the foams. The stress−strain curves, in compression mode, were obtained at room temperature on disks having 30 mm of diameter and 15 mm of thickness. A crosshead speed of 15 mm min$^{-1}$ was used.

A Hitachi scanning electron microscope was used to observe the cellular structure of the foams. The samples were fractured after immersion in liquid nitrogen, and the material was coated with a thin layer of gold before the observations.

## RESULTS AND DISCUSSION

### Polymerization Kinetics

The effect of starch content and catalyst concentration on the polymerization kinetics were evaluated separately. Due to the high exothermic behavior and the relatively fast reaction, it is possible to monitor the polymerization kinetics through the measure of the temperature. The degree of reaction $\alpha$ can be calculated by the following expression:

$$\alpha = \Delta T/\Delta T_{\max} \tag{1}$$

where $\Delta T$ is the difference between the actual and the initial temperature, and $\Delta T_{\max}$ is the
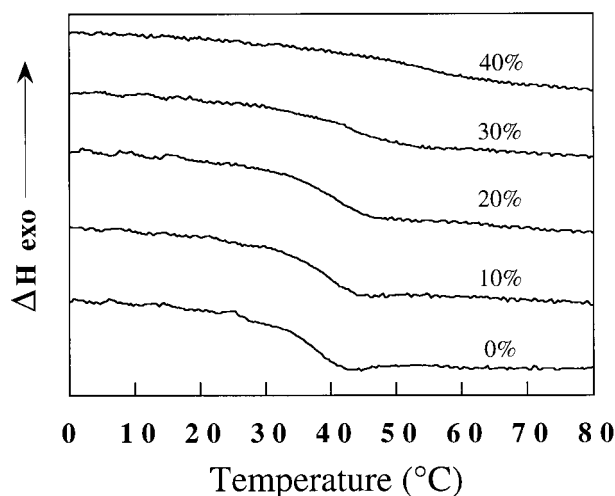


**Figure 3** Differential scanning calorimetry curves of starch-based PU foams. Percentage is referred to starch in the S/PCLt mixture.

**Table II  Effect of Composition on Glass Transition Temperature and Thermal Stability**

| S/PCLt/PEG | $T_g$ (°C) | $T_A$ (°C) | $T_N$ (°C) |
|---|---|---|---|
| 0/100/0 | 39.3 | 324 | 337 |
| 10/90/0 | 40.7 | 321 | 334 |
| 20/80/0 | 43.5 | 316 | 330 |
| 30/70/0 | 47.4 | 311 | 325 |
| 40/60/0 | 54.3 | 309 | 323 |
| 30/45/25 | 32.6 | — | — |
| Starch | — | 299 | 307 |

$T_A$ and $T_N$ are the peak temperatures of the weight loss derivative of the thermogravimetric curves in air and nitrogen flux.

maximum difference of temperature observed during the reaction.

The effect of starch content on the polymerization kinetics is shown in Figure 1. The curves display a gradual increase of temperature up to 20 s, followed by a fast growing of $\alpha$ as function of time. This behavior, usually observed during the formation of PU foams,[27] can be explained on the basis of the reaction mechanisms occurring during the foam formation. At the early stage of the polymerization, bubble nucleation results from dissolved gases in the monomer and dispersion of air or other gases induced by the mechanical mixing. This phenomena goes with a slow increase of temperature and, as shown in Figure 1, it occurs in the first 10–15 s of the reaction. Nucleated bubbles will then grow due to the generation of carbon dioxide produced by the isocyanate–water reaction. The gel keeps expanding, and the foam will rise reaching the final volume. Foam rise is associated with a sharp increase of temperature, and maximum values were reached after 25 s for the PU foam without starch, and 35 s for the PU foam containing 30% starch. This difference is probably due to the larger molecular weight of the polysaccharide that results in a higher viscosity of the polyol mixture causing a delay in nucleation. Moreover, the greater viscosity of the expanding gel affects the reaction rate of the following stage, which is confirmed by the lower slope of the curve in the linear zones above $\alpha = 0.2$ for the samples containing starch.

The effect of the dibutyltin dilaurate concentration on the reaction kinetics of foams obtained from a polyol containing 30% polysaccharide is shown in Figure 2. The reduction of the amount of catalyst from 0.8 to 0.4 pphp resulted in a high

decrease of the reaction rate, and the time needed for the completion of the foaming varied from about 40 to 450 s. Experimental data were also obtained on foams containing a reduced amount of amine catalyst. The unmodified reaction rate observed in this case suggests that the polymerization kinetics can be optimized mainly by adjusting the concentration of dibutyltin dilaurate.

**Thermal Analysis**

Calorimetric curves (second scans) of the foams as a function of the starch content are reported in Figure 3. The glass transition temperatures of these PUs increase from 40°C to 55°C (Table II) and higher $T_g$'s are related to greater amounts of starch in the initial composition. This is the first evidence that starch participates in the chemical reaction, becoming part of the macromolecular structure. The increase of $T_g$ suggests that the molecular mobility of these PUs is reduced by the addition of the polysaccharide, and an effect on the mechanical properties can be expected. The formulation containing PEG showed a decrease of $T_g$ (Table II) and, as will be shown later, it will contribute to increased flexibility of these foams.

Thermogravimetric curves, reported as the derivative of the weight *versus* temperature for the samples tested in a nitrogen flux, are shown in Figure 4. The temperature that corresponds to the maximum in the derivative curve decreases when the amount of starch in the PU formulation increases. Similar behavior was observed in tests
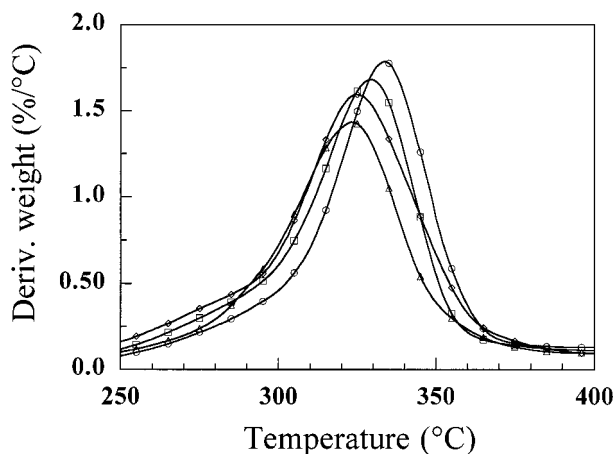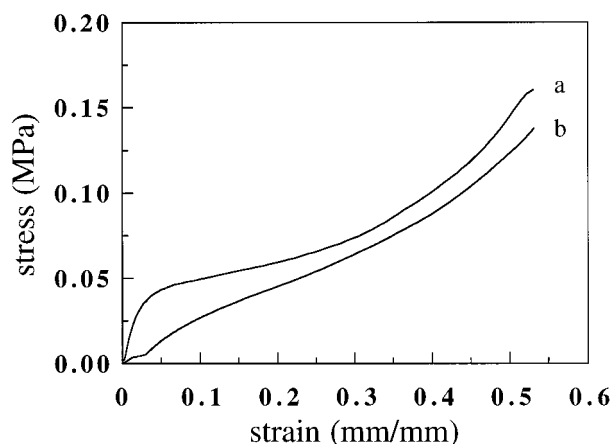


**Figure 4**  Effect of starch content on thermal stability under nitrogen flux. (S/PCLt: 10/90, 20/80, 30/70, and 40/60). Temperature of the main peak decreases by increasing the amount of starch.
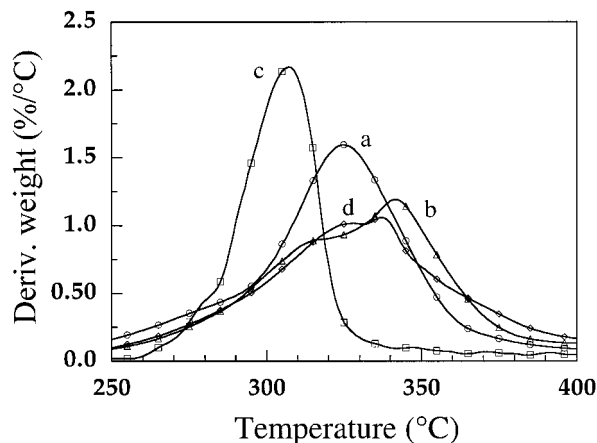
**Figure 5** Thermogravimetric analysis of: (a) PU foam S/PCTt 30/70; (b) PU foam S/PCLt 0/100 + starch; (c) pure starch; and (d) PU$_{PCL}$.

**Table III  Effect of Composition on Density and Compressive Modulus: Minimum and Maximum Experimental Data for $\rho_f$ and $E_f$ and Minimum and Maximum Values Predicted for $E_s$**

| S/PCLt/PEG | $\rho f$ (kg m$^{-3}$) | $E_f$ (MPa) | $E_s$ (MPa) |
|---|---|---|---|
| 0/100/0 | 125 ÷ 155 | 0.46 ÷ 0.54 | 19 ÷ 35 |
| 10/90/0 | 101 ÷ 119 | 0.45 ÷ 0.49 | 35 ÷ 47 |
| 20/80/0 | 88 ÷ 112 | 0.96 ÷ 1.02 | 81 ÷ 123 |
| 30/70/0 | 81 ÷ 89 | 0.76 ÷ 0.88 | 111 ÷ 150 |
| 40/60/0 | 60 ÷ 70 | 0.60 ÷ 0.68 | 106 ÷ 166 |
| 30/45/25 | 85 ÷ 115 | 0.27 ÷ 0.43 | 32 ÷ 37 |

performed in air flux, and the temperatures related to the peaks are reported in Table II. To evaluate the effect of the polysaccharide on the thermal degradation of these materials, thermogravimetric analysis was also performed on pure starch, and on PU foams synthesized only from PCLt as polyol (PU$_{PCL}$); the results of these tests are reported in Figure 5. Curve $a$ is referred to the behavior of a PU foam having a composition of S/PCLt 70/30; curve $b$ is obtained from the analysis of a sample containing PU$_{PCL}$ and starch whose amount is such that the ratio S/PCLt is kept equal to the ratio 70/30, as in the PU starch-based foam. Even though the polysaccharide content is the same in the two experiments, the reaction of starch with isocyanate results in the pres-

ence of a single degradation peak at 325°C (curve $a$). The addition of unreacted starch to the test chamber produces a main degradation peak (341°C) related to the degradation of the foam PU$_{PCL}$, and a shoulder ($\sim$ 310°C) connected to the thermal degradation of starch granules. A proof of the above assumption is given by the analysis of the thermogravimetric curves of pure starch (curve $c$) and of the foam PU$_{PCL}$ (curve $d$). The degradation peaks of these two curves, reported in the same figure, are connected to the shoulder and the peak in curve $b$.

The absence, either under air or nitrogen flux, of two peaks for the starch-based PU foams synthesized (Fig. 4) is more evidence that a reaction between starch and isocyanate occurred. The slight reduction of the degradation temperature, which is about 15°C for the composition of S/PCLt 40/60 indicates that the thermal stability of these foams are not substantially affected by the presence of starch.

## Mechanical Properties and Morphology

The compressive stress−strain curves of two representative foams are reported in Figure 6. Curve a is related to PU foams containing 30% of starch and 70% of PCLt, whereas curve b refers to materials synthetized from a polyol containing 30% starch, 45% PCLT, and 25% PEG. Curve a shows the typical behavior of plastic foams characterized by an initial linear portion, related to the elastic deformation of cells, a plastic yield, and a densification part characterized by a progressive increase of the stress *versus* strain. This behavior was observed for all of the foams without PEG, and the related values of the modulus, calculated as the slope of the linear part, are reported in Table III. An increase of the starch content pro-



**Figure 6** Stress−strain curves of the foam: (a) S/PCTt/PEG 30/70/0 and (b) S/PCTt/PEG 30/45/25.
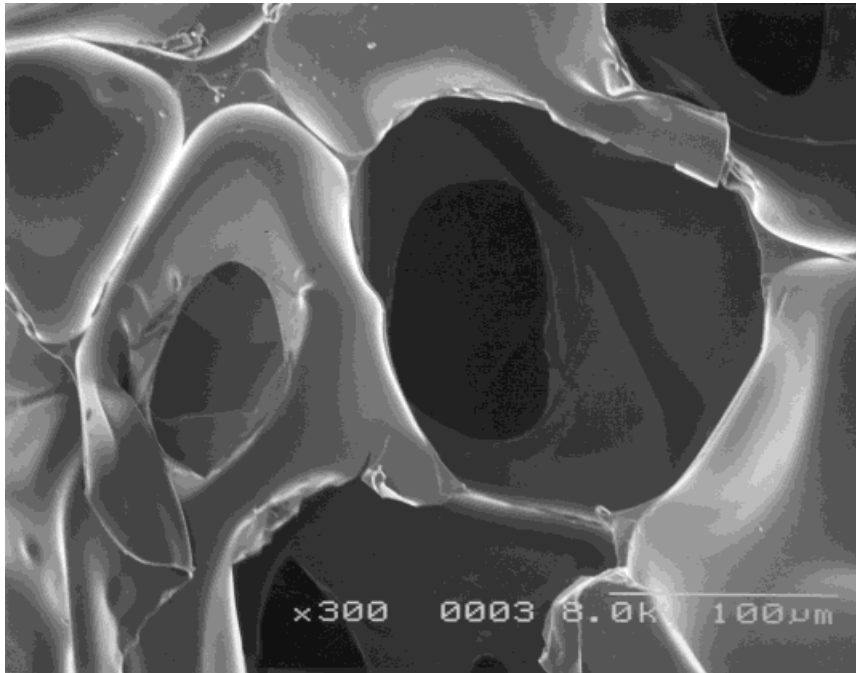
**Figure 7**    Fracture micrograph of the foam S/PCTt/PEG 30/70/0.

duces an initial increase of the modulus from 0.54 MPa to 1.02 when starch is added up to 20%. This trend is followed by a reduction of these values up to 0.68 MPa, when the content of starch reaches 40%. The explanation of this behavior is related to the variation of the foam density that was observed for the different compositions. In Table III are reported the average values of density of the materials analyzed.

It has been shown that it is possible to correlate the mechanical properties of open-cell foams and those of the pure polymer through the following relationship[28]:

$$E_f = E_s(\rho_f/\rho_s)^2 \qquad (2)$$

where $E_f$ is the modulus of the foam; $E_s$ is that of the material itself; and $\rho_f$ and $\rho_s$ are, respectively, the foam and the material density. Assuming $\rho_s = 1000 \, (\text{kg m}^{-3})$, the previous relationship allows the estimation of the material modulus. As reported in Table III, $E_s$ increased from 35 to 166 MPa. These results are in agreement with the previous observations regarding the glass transition temperature of the materials, because an increase of the $T_g$ is usually accompanied by an increase of the material modulus. Analogous comments can be drawn on the foams containing PEG.

In this case, the presence of PEG in the macromolecular structure produces a reduction of $T_g$ and, as a consequence, an increase of the flexibility of the material, as shown by the results reported in Table III and by curve II in Figure 6.

The hypothesis of the open-cell structure is confirmed by the morphological analysis performed by scanning electron microscopy. Figure 7, relating to a foam of composition S/PCLt 30/70 is representative of the typical morphology of these foams. All of the materials studied showed a homogeneous structure without evidence of macroscopic phase separation.

## CONCLUSIONS

Starch-based PUs were synthesized, and their thermal, mechanical properties, and morphology were analyzed. Polymerization kinetics is slightly affected by the starch content, and the reaction rate can be optimized by controlling the catalyst concentration.

Calorimetric and thermogravimetric analyses proved that starch participates in the chemical reaction, inducing an increase of the glass transition and a decrease of the thermal stability of the materials. These chemical modifications produce

an increase of the material modulus and, at the same time, a reduction of density of these open-cell foam densities.

The properties of these foams can be modulated by the addition of a certain amount of PEG which, introducing flexible chains in the macromolecular structure, reduces the $T_g$ of the materials and generates foams with higher flexibility.

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