# Cast Polyurethane Elastomers Obtained with N,N′-Ethyleneurea and 1,4-Butanediol as Chain Extenders

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**ABSTRACT:** Tensile properties and dynamic mechanical thermal properties for polyurethane elastomers extended with N,N′-ethyleneurea (EU) and 1,4-butanediol (1,4-BD) were investigated. Also gel permeation chromatography and extraction experiments for selected elastomers were performed. EU residues were introduced into polyurethane during prepolymer synthesis at 140°C. Such prepolymers with built-in EU residues were extended with 1,4-BD for different [NCO]/[OH] molar ratios. The use of EU chain extender produces in general polymers with inferior mechanical properties compared to the typical 1,4-BD based polyurethanes, although some of the EU-based polymers show improved strain-stress parameters. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 728–733, 2000

**Key words:** polyurethane elastomers; N,N′-ethyleneurea; DMTA

## INTRODUCTION

Polyurethane elastomers can be found in a variety of products, featuring a range in properties and performance. This is a result of the extensive choice of chemicals that may be used in their synthesis. The majority of polyurethane elastomers is, however, based on diisocyanates, long chain components such as polyesters and polyethers, and on short chain difunctional (or multifunctional) alcohols or amines, which act as chain extenders. Although the reaction of urea groups with isocyanates is one of the basic reactions, widely used in polyurethane curing processes,[1–3] urea derivatives are rarely used as chain extenders in the syntheses of polyurethanes. This seems to be a consequence of their low reactivity and the fact that they require relatively high temperatures for the formation of biuret groups.[4,5] Only a few papers concerning the use of N,N′-ethyleneurea and other N,N′-disubstituted urea derivatives were found.[6–11] Our intention was to learn more on the influence of this type of chain extender on selected polyurethane system.

In this work we present tensile properties, dynamic mechanical thermal analysis (DMTA), and gel permeation chromatography results for some cast polyurethane elastomers containing different amounts of EU residues.

## EXPERIMENTAL

Due to the high melting temperature of N,N′-ethyleneurea (EU) (128°C), the following routine was established: initially, the prepolymer reacted at 140°C with EU (0.1–0.5 mol of EU per 1 mol of prepolymer). Subsequently 1,4-BD was added at 90°C to extend the prepolymer completely. In our earlier paper[12] we initially let 1 mol of the prepolymer react with 0.5 mol of EU for 2, 4, and 6 h.

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**Table I   Parameters of Prepolymers Containing EU Residues**

| Prepolymer Name | Molar Ratio PEBA/MDI/EU | $[NCO]_0$ (%) | $[NCO]_H$ (%) | $[NCO]_{EU}$ (%) | Degree of Conversion (%) |
|---|---|---|---|---|---|
| PREU-0 | 1.000/5.090/0.000 | 10.5 | 10.4 | 10.4 | — |
| PREU-10 | 1.000/5.440/0.444 | 11.1 | 11.1 | 10.0 | 100 |
| PREU-20 | 1.000/5.090/0.818 | 10.5 | 10.4 | 8.3 | 100 |
| PREU-30 | 1.000/5.150/1.245 | 10.6 | 10.5 | 7.3 | 100 |
| PREU-50 | 1.000/5.500/2.250 | 11.2 | 11.1 | 6.7 | 83 |

$NCO_0$ is concentration of isocyanate groups in starting prepolymer; $NCO_H$ is concentration of isocyanate groups in starting prepolymer after annealing in 140°C; $NCO_{EU}$ is final concentration of isocyanate groups in prepolymer containing EU residues; degree of conversion is the degree of conversion for EU in the reaction with the starting prepolymer calculated from the equation: $100 \times [(1 - c/100) \times NCO_H]/NCO_{EU}$, where $c = [MDI(mol) - PEBA(mol)]/EU(mol)$.

Longer reaction times significantly improved mechanical properties of the elastomers. The synthesis and the properties of EU- (and also $N,N'$-etylenethiourea-) based polymers obtained in polar solvents are presented elsewhere.[13]

EU reacts with isocyanate groups typically, giving as a result biuret group derivatives.

## Materials

4,4′-Diphenylmethane diisocyanate (MDI), (ICI) was melted and filtered at 60°C. The poly(ethylene-butylene adipate)diol (PEBA), ($L_{OH} = 56$, Chemical Works "Zachem," Bydgoszcz, Poland), was dried in a reactor with a mechanical stirrer at 80°C, under a vacuum of ca. 250 Pa, during 6 h. $N,N'$-ethyleneurea (2-Imidazolidone) (EU) (Fluka AG) was dried for 10 h at 70°C in a vacuum oven (250 Pa). 1,4-Butanediol (1,4-BD) (BASF) was dried for 4 h at 50°C in a vacuum oven (250 Pa).

## Preparation

### The Synthesis of the Prepolymer

A predetermined quantity of MDI was added to PEBA at 80°C, such that the molar ratio of NCO to OH groups was approximately 5.1:5.5. The reaction forming the prepolymer was carried out for 15 min at 90°C. Then, the prepolymer was heated within 10 min up to 140°C and simultaneously degassed under vacuum (250 Pa). The reactor was unsealed and the appropriate quantities of EU varying from 0.45 to 2.25 mol were added. The reactor was sealed again and heating was continued for 2 h at 140°C. The obtained prepolymer containing EU residues (PREU) was left for 12 h at 20°C and subsequently used for the polyure-

thane synthesis. The parameters of all PREU syntheses are shown in Table I.

### The Synthesis of Polyurethanes

PREU was heated to 90°C and then mixed within 10–30 s with 1,4-BD. The quantity of 1,4-BD was chosen such that molar ratios of NCO to OH groups ranging from 0.80 to 1.30 were obtained. One hundred and fifty grams of the mixture was placed in a centrifuge drum running at a speed of ca. 3500 rpm. The formation of elastomers was carried out for approximately 30 min at 90°C. All the elastomers were postcured at 100°C for 24 h. The specimens which were obtained were 1.5-mm thick.

Samples of polyurethanes were named accordingly to the name of prepolymer they were based on: PUEU-0, PUEU-10, . . ., PUEU-50.

## RESULTS

### Mechanical Properties

Selected results of mechanical testing are shown in Figure 1 and Figure 2. The presence of EU residues in the samples has a significant influence on tensile strength and elongation at break. In general, they both decrease with increasing amount of EU added to the prepolymer. The poorest mechanical results were observed for the samples obtained with PREU-50. The tensile strength at break (Fig. 1) for PUEU-10 and PUEU-0 shows similar characteristics. The outstanding values for PUEU-10 for elongation at break (Fig. 2) should be noticed. They exceed the values observed for the samples obtained without EU
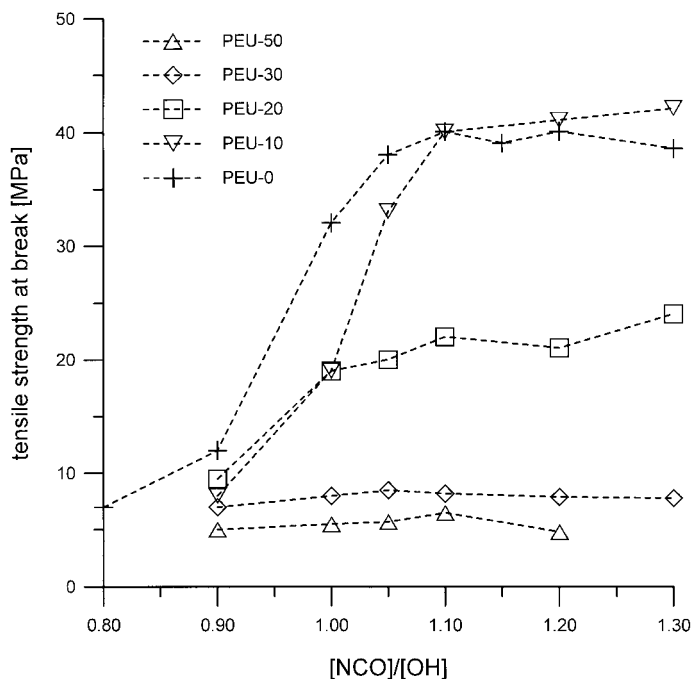
**Figure 1**    Variation of the tensile strength at break with the molar ratio of $[NCO_{PREU}]$/$[OH_{1,4-BD}]$ for the investigated PUEU elastomers.

(PUEU-0) as well as for the samples with higher content of EU. For the samples containing the largest amounts of EU, the maximum of the elongation could be found for the highest values of [NCO]/[OH] molar ratio. For all the elastomers, permanent elongation after break did not exceed 100%.

### Dynamic Mechanical Thermal Analysis Properties

The measurements were performed using a Polymer Laboratories DMTA Mark III analyzer with a standard bending head at a frequency of 1 Hz and scanning rate of 4 deg/min in a double cantilever geometry. The temperature dependence of the loss tangent and the storage modulus for PUEU-0, PUEU-20, and PUEU-50 are presented in Figure 3. All investigated elastomers were synthesized with a molar ratio of [NCO]/[OH] = 1.10. The tan $\delta$ peak of $\alpha$ relaxation of the polyester soft segments was found for PUEU-0 at $-17.5°C$, for PUEU-20 at $-15.6°C$ and for PUEU-50 at $5.7°C$. An increasing amount of EU results in an increasing glass transition temperature of the soft segments. The shape of $\alpha$ relaxation peak varies with different EU contents. It is sharp and distinctive for PUEU-0 and almost flat for PUEU-50. The

amount of EU affects significantly the softening points of the polymers and the storage modulus profiles. The $E'(T)$ curve imparts a typical glass-transition saddle and another drop at the softening temperature area ($\sim130°C$) for the sample PUEU-0 obtained without EU. For PUEU-50 one can observe constant, linear softening, which starts at the glass transition temperature. The melting point was observed approximately at $110°C$. $E'$ values of PUEU-20 lie between the results of PUEU-50 and PUEU-0.

### Extraction and Gel Permeation Chromatography Experiments

For extraction and gel permeation chromatography (GPC) experiments the elastomers were synthesized with a molar ratio of [NCO]/[OH] = 1.10. All PUEU samples were extracted with acetone for 24 h in typical soxhlet apparatus. The results of the extraction experiments are shown in the upper part of Table II. A higher content of EU in PUEU increases the amount of the soluble part of the elastomer. For PUEU-50, 66% of its weight could be removed with acetone. This amount is tree times higher then the one recorded for PUEU-0.
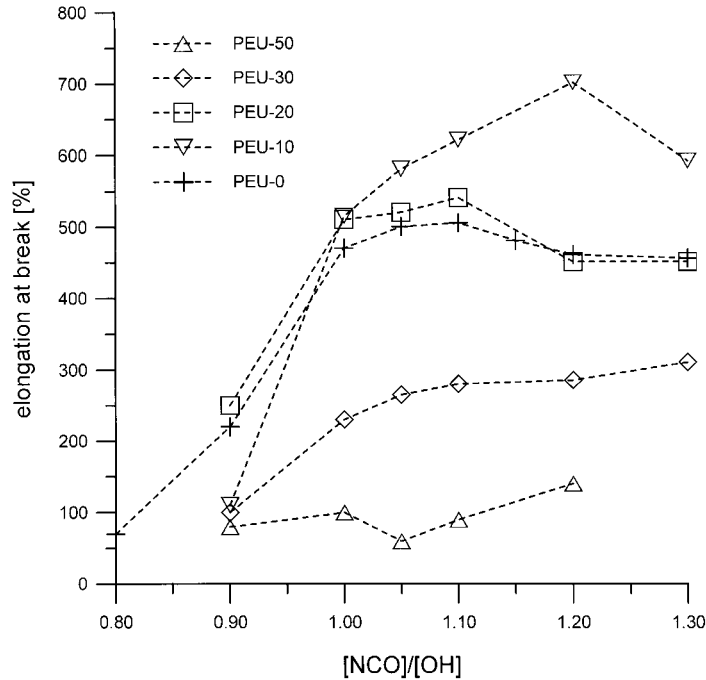
**Figure 2**  Variation of the elongation at break with the molar ratio of $[NCO_{PREU}]/[OH_{1,4\text{-}BD}]$ for the investigated PUEU elastomers.

GPC experiments were carried out on a Waters 600-MS chromatograph, equipped with a refractometric detector. The instrument was calibrated for polystyrene. Tetrahydrofuran was used as eluent. The results are presented in the bottom part of Table II. $M_n$ drops dramatically when EU is introduced into the elastomer. $M_n$ is less then half for PUEU-10 compared with PUEU-0. For
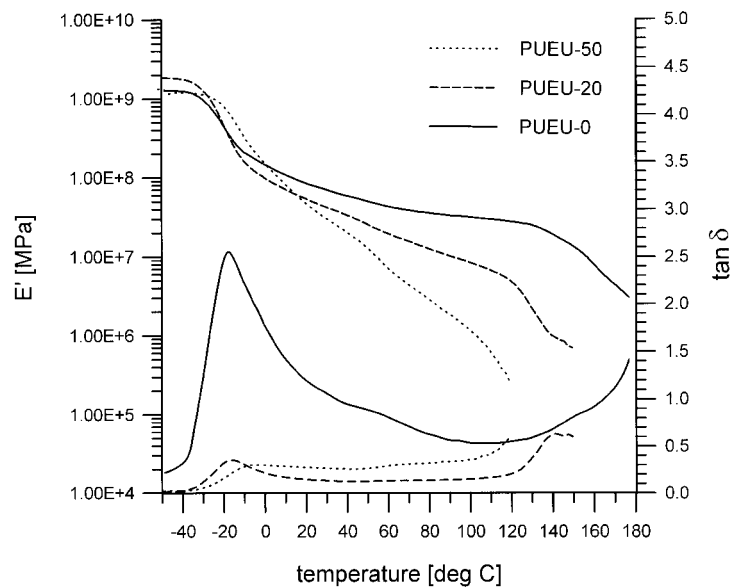


**Figure 3**  Variation of the loss tangent ($\tan \delta$) and storage modulus ($E'$) with temperature for selected elastomers.

**Table II   The Extraction and GPC Data**

| Symbol of the sample | PUEU-0 | PUEU-10 | PUEU-20 | PUEU-30 | PUEU-50 |
|---|---|---|---|---|---|
| Acetone soluble fraction (%) | 19 | 20 | 26 | 31 | 66 |
| $M_n$ | 58300 | 25500 | 26900 | 13000 | 9600 |
| $M_w$ | 187700 | 39700 | 115700 | 43900 | 21800 |
| $M_w/M_n$ | 3.218 | 1.56 | 4.29 | 3.36 | 2.28 |

the elastomer with the highest content of EU (PUEU-50) $M_n$ is over six times lower than for PUEU-0. The maximum $M_w$ was observed for PUE-20.

## DISCUSSION

The molecular mass measurements and the extraction experiments suggest the presence of relatively low molar mass, oligomeric structures in the EU-based elastomers. It is shown that the acetone-soluble fraction increases and molar masses drop significantly with increasing EU content in the elastomer. The oligomers are probably products of mono- or diaddition of EU with NCO-terminated polyester chains. Although the degree of EU conversion for PUEU-10, PUEU-20, and PUEU-30 reached 100%, it is still uncertain how much of the EU was completely built in. At 140°C some other reactions may occur leading to allophanate and biuret linkages. Therefore, even for 100% conversion the oligomeric structures may still be present. For DMTA tan δ profiles a sharp and distinctive peak of the soft segment α relaxation, which indicates a good soft-hard segments microphase separation.[14,15] For all the samples containing EU residues, the tan δ peak is significantly less pronounced comparing with the peak for the sample based only on 1,4-BD. This suggests that for the EU elastomers, soft phase domains are not well organized and a soft-hard segments phase intermixing occurs. For the rubbery region, the nonflat storage modulus-temperature profiles indicate that also the hard segments domains of EU elastomers are poorly developed. Strong interaction within hard segments domains (mainly hydrogen bonds) usually stabilize the elastomer structure at higher temperatures. This is the case with the PUEU-0 elastomer, which exhibits the most flat rubber plateau region among the investigated polyurethanes. The DMTA storage modulus profiles for both EU-based elastomers show that the phase mixing and

hard segment domain disorder increase with increasing the EU residues contents. The results presented for the EU elastomers also indicate a lack or a low level of chemical crosslinking as the chemical bonding also should stabilize the polymer structure at higher temperatures. We suspect that the previously mentioned oligomers can play an important role in the phase separation process. They can act partially as a soft-hard phases compatibilizer or plasticizer leading to a higher phase degree of intermixing. For the PUEU-10 series the values of tensile strength at break are similar to those obtained for PUEU-0. The elongation at break of PUEU-10 samples are superior to PUEU-0 and all other samples. We suppose that all the chain extender is built into the backbone almost completely when small contents of EU are employed, thereby reducing the amount of oligomers. For higher contents of EU residues, a significant deterioration of the investigated mechanical properties is observed, also indicating a low level of phase separation.

## CONCLUSION

Series of polyurethane elastomers with different amount of EU residues were prepared. The introduction of EU residues into polymer structure causes the deterioration of their tensile properties and (for higher content of EU) deterioration of the elongation at break values. The samples with the smallest amount of EU possessed higher values of the elongation at break compared with the elastomer synthesized without EU. The introduction of EU residues was accompanied by the formation of urethane oligomers that were easily soluble in acetone.

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