The effect of plasticization on the functional properties of thermoplastic polyurethane ureas

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Abstract. Several series of plasticized segmented polyether urethane of linear structure which can be used as the polymer base of thermoplastic materials were synthesized. The possibility of obtaining thermoplastic segmented polyurethane ureas with a softening temperature of 100 ±120°C when using isophorone diisocyanate as the main element for building polymer chains, and DEHS as a plasticizer was proven. The original method for the purification of aromatic amine 4,4′-methylene-bis(2-chloroaniline) used in the process of synthesizing polyurethane ureas as a chain extender was developed. The polymers obtained have a uniquely low glass transition temperature close to -100°C with a plasticizer concentration of not more than 40%. The strength of these materials is more than 10 MPa at room temperature, and it is more 40 MPa at -70°C.

1. Introduction

Frost-resistant materials are necessary to manufacture elastic elements of machines and mechanisms that work under conditions of the Arctic climate, maintaining a highly elastic state down to -70°C. The most well-known manufacturer of polyurethanes BASF (Germany) developed a series of high strength thermoplastic polyether urethanes of the Elastollan type. Some series of Elastollan were widely used in Arctic especially with a plasticizer (esters of terephthalic acid). But the glass transition temperature of such materials is not lower than -50°C. This is unacceptable for extreme climatic conditions of the Arctic areas.

Earlier, interesting cross-linked urethane-containing elastomers with the temperature of structural glass transition lower than -90°C were developed for free casting processing [1]. The new materials are 2-2.5 times greater in strength than the existing analogues and workable in a wide temperature range. However, to ensure the mass production of frost-resistant urethane-containing elastomers, it is necessary to solve the problem of developing thermoplastic urethane-containing block copolymers without prejudice to their functional properties.

The purpose of this work is the synthesis of urethane-containing block copolymers and the study of the influence of plasticization on their properties, the identification of structural factors and prescription factors providing the softening temperature of the hard phase of not more than 170°C and the glass transition temperature of the polymer matrix close to -90°C.

The work is based on ideas about the possibility of obtaining thermoplastic polyurethane ureas based on linear polyethers with terminal hydroxyl groups, diisocyanates and aromatic amines.
The possibility of regulating most important characteristics of the mentioned polyurethane ureas using plasticization should be preserved during synthesis. We can use various esters of organic polycarboxylic acids and esters of some non-organic acids as plasticizers.

Unlike similar casting compounds with spatially cross-linked structures, the synthesis of linear polymers with thermoplastic properties should preclude the formation of three-dimensional structures. This demand was provided in the present work by a chemical method using the molar ratios between the free isocyanate groups of intermediate prepolymers and the complementary amine groups of the chain extender lower than 1 at the synthesis (NCO/NH$_2$<1).

The effectiveness of plasticization for the regulation of the most important functional properties of polyurethanes and polyurethane ureas has been proven earlier [1-3]. Di(2-ethylhexyl) sebacate DEHS, was chosen as a low-polar plasticizer to substantially reduce the glass transition temperature of the soft phase of urethane-containing elastomers. This plasticizer does not adversely affect the microphase separation in nano-heterogeneous elastomers [4]. The glass transition temperature of DEHS is -107°C.

2. Materials and Methods

Segmented polyurethane ureas (SPUUs) based on oligoether polyfurite 1400 (polybutylene oxide diol), plasticized with DEHS, were chosen as objects of study. The value of the molecular mass of this oligomer $M_r$≈1400 g mol$^{-1}$ was chosen earlier taking into account its non-crystallisability [1].

SPUUs were obtained by a two-stage technology through the synthesis of prepolymers based on the selected polyether — polyfurite 1400, 2,4-tolune disocyanate (TDI) or isophorone disocyanate (IPDI) and the subsequent curing of the prepolymers using mixtures containing the diamine chain extender MOCA (4,4′-methylene-bis(2-chloroaniline)) and a variable amount of the DEHS plasticizer (from 15 to 40%). The synthesis of SRT-1 series was provided using TDI, the same of SRT-2 series was provided using IPDI.

The molar ratio between the isocyanate groups of the prepolymer and the amine ones of MOCA at the curing reaction was 0.95. Samples of SPUU were cured for 3 days at 80°C. Completeness of the conversion of NCO-groups of the prepolymers was controlled by the method of IR-Fourier spectroscopy on a Bruker Vertex 80v installation.

It should be noted that SPUUs synthesized previously on the base of the mentioned MOCA showed that their softening temperature is in the area of 205±210°C when using TDI, and the same is in the area of 152±162°C when using IPDI.

Mechanical tests of the synthesized samples were carried out at 23°C using the universal testing machine INSTRON 3365. The engineer strength $\sigma$ (maximum stress calculated on the initial section of the sample), relative critical deformation $\varepsilon_{cr}$, engineering modulus $E_{100}$ were determined at the tensile rate 0.56 s$^{-1}$. The glass transition temperature of the soft phase of materials $T_g$ was determined by the DSC-method using a DSC 822e differential scanning colorimeter from METTLER TOLLEDO. The softening temperature of the hard phase $T_h$ was determined by the thermo-mechanical analysis method using a TMA/SDTA 841e installation manufactured by METTLER TOLLEDO at a scan rate of 0.05 degrees·s$^{-1}$ under a load of 0.015 MPa.

A new laboratory method was developed for purification of the MOCA diamine to investigate the possibility of obtaining materials of improved quality. Purification of MOCA was based on its recrystallization from n-octane. The dissolution in octane was carried out at 90°C, the separation of the phases at the same temperature. The average yield was 61%.

Inspection of the purified MOCA was carried out in comparison with the original product (trademark Kuralon M from Brenntag, Sweden). It was found that the purified sample has a higher frequency degree: analysis of 1H and 13C NMR spectra recorded on a Bruker Avance-Neo 400 spectrometer in acetone-d$_6$ and using hexamethyldisiloxane (0.055 ppm) as an internal standard at room temperature, proved that in addition to the signals of 4,4′-methylene bis(2-chloroaniline):

- 1 H NMR (acetone-d$_6$, 400 MHz): $\delta$ 3.61 (s, 2H, CH2), 4.00 (c, 4H, NH2), 6.69 (d, 3J = 8.0 Hz, 2H, 4C, 15C), 6.80 (dd, 3J = 8.0 Hz, 4J = 1.6 Hz, 2H, 3C, 14C), 6.96 (s, 2H, 6C, 11C) ppm;
- 13 C NMR (acetone-d6, 400 MHz): δ 40.42 (CH2), 117.09 (3C, 14C), 119.34 (1C, 12C), 129.41 (4C, 15C), 130.35 (5C, 10C), 132.75 (6C, 11C), 143.76 (2C, 13C) ppm, in sample No.1, additional signals are present, namely, in the 1H NMR spectra - 3.69 ppm, 4.32 ppm, 6.90 ppm, in the 13C NMR spectra - 37.76 ppm, 127.94 ppm, 128.59 ppm, 129.22 ppm, 130.20 ppm, 130.88 ppm, 132.42 ppm, 143.94 ppm, which indicates the presence of impurities in the original sample.

These impurities contain methylene (3.69 ppm) and amino (4.32 ppm) groups, by nature different from methylene (3.61 ppm) and amino (4.00 ppm) groups in 4,4′-methylene-bis(2-chloroaniline) in its structure, as well as additional protons of the phenyl ring. The above analysis suggests that the impurity is 4-(4-aminobenzyl)-2-chloroaniline, which differs from 4,4'-methylene-bis(2-chloroaniline) by the presence of only one chlorine atom in the structure.

The results of the elemental analysis (carried out on the CHNS-932 instrument of LECO Corporation) of the purified product are presented below in Table 1. They show the above mentioned impurity was completely deleted during the purification.

### Table 1. Results of the elemental analysis for the original MOCA sample, and the same after purification.

| MOCA          | Content of elements, % |
|---------------|------------------------|
|               | C  | H  | N  |
| Purified sample| 58.92 | 4.42 | 10.33 |
| Initial sample | 59.00 | 4.38 | 10.17 |
| Theoretical value | 57.57 | 4.42 | 10.33 |

The purified sample of MOCA, which was characterized by complete coincidence of the experimental content of nitrogen and hydrogen, was used for synthesis of polyurethane ureas of the SRT-1 and SRT-2 series.

### 3. Discussion

DSC-thermograms obtained for the SPUM samples show a consistent decrease in the glass transition temperature of the polymer matrix as the content of plasticizer in it increases (figures 1, 2). Also one can clearly see the effect of the partial crystallization of DEHS in the thermograms of samples synthesized using TDI in the region close to 0°C (figure 1). On the one hand, this indicates an insufficiently high thermodynamic stability of the SPUM-DEHS systems synthesized using this disiocyanate, on the other hand, the thermal effect is relatively insignificant (no more than 10 J·grad⁻¹).

![Figure 1](image1.png)  
Figure 1. DSC-thermograms for SRT-1 series at various DEHS concentration: 1 – 0%, 2 – 15%, 3 – 30%, 4 – 40%.

![Figure 2](image2.png)  
Figure 2. DSC-thermograms for SRT-2 series at various DEHS concentration: 1 – 0%, 2 – 15%, 3 – 30%, 4 – 40%.

However, the presence of this effect indicates that SRT-1, when cured in usual conditions (80–90°C), forms hard blocks with a dense structure, which leads to a decrease in the thermodynamic affinity of the polymer matrix as a whole to the plasticizer used. Table 2 shows the obtained values of the glass
transition temperature of the polymer matrix and the softening temperature of the hard phase of these samples. All synthesized polyurethane urea samples were soluble in tributyl phosphate, which proves their linear structure [4].

| С, % | Т,°С | С, % mas. | Т,°С |
|------|------|-----------|------|
| 0    | -66  | 0         | 206  |
| 15   | -79  | 15        | 203  |
| 30   | -92  | 30        | 209  |
| 40   | -101 | 40        | 207  |

As it has been determined, the use of IPDI as a diisocyanate is most promising. The softening temperatures for samples of the corresponding SRT-2 series were significantly lower than for ones obtained on the base of TDI (table 2). The strain-stress behavior of all the obtained linear polyurethane ureas in a wide temperature range corresponds to highly elastic materials. One can see in figure 3 not only the stretching curves typical for the cast polyurethane ureas (curves 1’ – 4’), but also curves with hardening (1 – 4), whose appearance indicates the development of reversible structuring during strain, which is extremely important for obtaining high strength characteristics [5, 6].

This allows us to recommend these materials for further development in the direction of increasing the strength characteristics using both chemical factors and the introduction of reinforcing fillers.

The higher softening temperatures of SRT-1 samples synthesized on the basis of TDI, exceeding 200°C, are close to the upper temperature limit for the processing of thermoplastic polyurethanes (210°C). Processing of such materials is possible under the conditions of preventing the oxidation of the processed materials (minimal contact with oxygen in the air).

Figure 3. Stress versus strain plots for SRT-2 (curves 1 – 4) and SRT-1 (curves 1’ – 4’) samples at 25°C. Curves 1, 1’ correspond to samples without plasticizer, other ones correspond to samples with DEHS: 2, 2’ for 15%, 3, 3’ for 30%, 4, 4’ for 40%.

Figure 4. Dependence of the strength on the content of plasticizer at different temperatures for SRT-1 and SRT-2 series: -70°C (1, 1’), 23°C (2, 2’), 40°C (3, 3’). The better manufacturability of thermoplastic SRT-2 based on isophorone diisocyanate is evident, which determines the great prospects of the respective materials. These materials with a high content of plasticizer (30-40%) showed excellent strength and high ability to strain (εk > 200%) at -70°C (figure 4). The same materials show excellent strength properties at room temperature as well: 5.8-8.6 MPa for...
SRT-1 samples and 9.7+10.0 MPa for SRT-2 samples. This is much higher than the strength level of comparable thermoplastic materials based on plasticized styrene-butadiene thermoplastic elastomers (2.2 MPa) [6].

The reasons for this phenomenon, in our opinion, are the peculiarities of the interaction of plasticizers with hard segments of polyurethane urea chains during their synthesis, namely the decrease in the concentration of hard blocks in the polymer matrix upon the introduction of a plasticizer not related to the geometric factor. In the very first approximation, when a plasticizer is introduced, all other things being equal, the elastic characteristics of the polymer (Young's modulus, engineer modulus, etc.) should change proportionally [7]:

\[ E = E_0 \phi_2 \]  

\( \phi_2 \) is the volume fraction of polymer in the plasticized sample; \( E, E_0 \) - engineer moduli of plasticized sample and of non-plasticized one, respectively. However, for both of the studied sample series, a decrease in the conditional modulus was observed with an effect far exceeding the geometric factor (figure 5).

![Figure 5. Dependence of the relative decrease in the engineer modulus on the plasticizer content for the SRT-1 (2) and SRT-2 (3) sample series. Curve 1 denotes the corresponding dependence taking into account only the geometric factor in accordance with equation (1).](image)

On the other hand, it is necessary to recognize that an increase in the content of plasticizer in the polymer system elevates the probability of premature chain termination of the polymer molecule growing during synthesis. This may be due to both the residual moisture content in the plasticizer after drying, and the content in the plasticizer of side impurities capable of interacting with free isocyanate groups.

The general view of the stress-strain plots in figure 3 indicates that the compositions based on IPDI have a high potential for the strain development, most clearly manifested in an non-plasticized sample (curve 1). This type of curves indicates the implementation of a “loose” structure of a hard phase in the described system, which is a potential source for obtaining improved physic-mechanical characteristics of the materials under study [5].

With an increase in the content of the plasticizer, the hardening effect decreases; it disappears when the content of the plasticizer is 30% or more. In our opinion, this fact indicates the dependence of the molecular mass of linear SPUU obtained during the synthesis on the plasticizer content.

4. Conclusion
Linear polyurethane ureas with thermoplastic properties were described at the first time. These polymers have uniquely low glass transition temperatures of the polymer matrix close to -100°C, with a DEHS plasticizer concentration of not more than 40%, with a strength of at least 10 MPa at room temperature and at least 40 MPa at -70°C.

Regularities of the mechanical behavior of plasticized polyurethane ureas with urethane and urethane urea blocks were determined in a wide range of temperatures (from -70 to 40°C).

A simple method was developed for purification for the widely used hardener for polyurethane urea compositions – MOCA (4,4’-methylene-bis(2-chloroaniline)). The purified MOCA can reduce the softening temperature of linear SPUU based on isophorone diisocyanate more than 20°C.
Thermoplastic polyurethane ureas based on isophorone diisocyanate plasticized with DEHS are recommended for use in the Arctic climate.

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