

## New Diurethane Plasticizers for Polyurethane Thermoplastics and Perspective Functional Composites

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**ABSTRACT:** A method to synthesize low-molecular-mass diurethane compounds via reaction between diisocyanates and various primary and secondary alcohols was presented. A number of diurethanes with the melting points below 100°C were revealed. These diurethanes can be used as fusible plasticizers for thermoplastic polyurethanes (TPU) and for high-filled composites based thereupon. TPU based on oligotetramethyleneoxide diol and on 4,4'-diphenylmethane diisocyanate and containing 30% of fusible diurethanes were produced. In the presence of such plasticizers, a 3-order increase in magnitude of the melt flow index was demonstrated. Data evincing significantly larger strength values of TPU and of tungsten-containing high-filled composites (94.2 wt %), comparing with thermoplastics plasticized with low-molecular-mass liquids, were presented. The mechanism of this phenomenon attributed to the partial crystallization of diurethanes in TPU compositions was described. Samples of low-toxic thermoplastic polyurethane having density value of 9.4 g/cm<sup>3</sup> and meant for protection of various facilities from radioactive radiation, instead of highly toxic metallic, lead, were prepared. Issues of improving the frost resistance of this new type of TPU were considered. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41481.

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### INTRODUCTION

Low-molecular-mass urethanes (or carbamates), as the products of reactions between isocyanates and alcohols, have been attracting the attention of researchers for years; the reason is that these urethanes combine the properties of both esters and amides.<sup>1</sup> They have been used as source components in organic synthesis,<sup>2</sup> as low-toxic pesticides,<sup>3,4</sup> as additives for inks,<sup>5,6</sup> and as greases.<sup>7</sup> Possibilities to use diurethane (biscarbamate) additives, that is, the products of interactions between diisocyanates and alcohols, as stabilizers of chemical resistance for polyurethanes and as regulators to control the melting point of hot-melt inks have been examined elsewhere.<sup>8,9</sup> Furthermore, liquid oligodiurethanes have been proposed to be used as nonmigrating plasticizers.<sup>10</sup>

The structure and properties of diurethanes based on two aliphatic diisocyanates and on various alcohols have been considered in detail elsewhere.<sup>11</sup> In our previous work, we demonstrated the possibility of using diurethanes based on 2,4-toluenediisocyanates as plasticizers of thermoplastic polyurethane binders in composites with high a micro-dispersive metal content.<sup>12</sup>

Polyurethanes represent a general class of polymers with various structures of polymer chains that contain urethane groups. They are used in many branches of industry and in medicine.<sup>13–18</sup> In practice, block-structured polyurethanes, segmented polyurethanes (SPUs), and polyurethane ureas (SPUUs) containing alternating hard and soft segments, which feature the best combination of properties, are most commonly used.<sup>13–20</sup>

Noticeable differences in the polarity of soft and hard segments of SPUs or SPUUs lead to their microphase separation with the subsequent formation of reinforcing fillers (5–30 nm hard domains).<sup>15,16</sup> Hydrogen bonds determine the structure and strength of structural formations in these materials.<sup>21–24</sup> Hard domains also play the role of cross-linking points in the physical network. This network proves to be more stable in the case of elevated temperatures, to mechanical loading and to low-molecular-mass liquids, as compared with labile networks of inter-chain physical bonds.<sup>25,26</sup> Significant amounts of various hydrogen-bonded associates in polyurethanes,<sup>20,27</sup> formation of micro-dispersive hard phases and the use of soft segments with various structures in these materials create prerequisites to control the properties of polyurethane materials.<sup>17,23,28,29</sup>

However, in view of the necessity to considerably vary the technological properties of thermoplastic binders containing large amounts of functional fillers (35–45 vol %), the variety of chemical structures of polyurethanes proves to be insufficient. Urethane-containing elastomers are known not to have high thermostability,<sup>30</sup> and the temperature of degradation usually starts around 180–200°C. This feature restricts the possibilities of processing segmented polyurethane thermoplastics (STPUs) with high filler contents. The use of large volumes of liquid plasticizers in polyurethane compositions to diminish their viscosity is usually ineffective, owing to appreciable deterioration of their mechanical properties.<sup>31–33</sup>

To create a new generation of thermoplastic polyurethanes (TPU), in our opinion, an approach based on the use of low-melting plasticizers appears to be more expedient. These compounds will reduce the viscosity of the polymers at temperature for STPU processing. At operational temperatures, a portion of such plasticizers will turn into the hard phase and can play the role of a reinforcing filler, in the way that nonorganic additives do.<sup>34</sup>

The ability to self-assemble (self-organization), that is, to form hydrogen bonds between diurethane particles and the polymer matrix, was laid down as an idea in which diurethanes are used as fusible plasticizers for polyurethane materials. The task to develop a new type of highly filled thermoplastic polyurethane involves the selection of plasticizers with suitable melting points (70–100°C). This selection may be more effective in the case of the availability a wide range of such compounds. In the framework of the set task, the synthesis and investigation of a large number of diurethanes is necessary, and this has been performed and is presented in this article.

In this article, the physical modification of STPU using fusible diurethanes is comprehensively examined. In addition, their effectiveness is appraised, as compared with conventional low-melting compounds and with chemically inert liquids such as proton acceptors. Particular attention is paid to the processing of STPUs containing high contents of a functional filler. The problem is solved by using high-density low-toxicity composites containing 94 wt % tungsten.

## EXPERIMENTAL

### Materials and Preparation of Specimens

To synthesize diurethane compounds, normal and branched alcohols (namely, 1-butanol, 2-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 3-methyl-1-butanol, phenyl-methanol, 2-methyl-1-propanol, 2-propanol, 2-methoxy-1-ethanol, 2-ethoxy-1-ethanol) and diisocyanates [2,4-toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), and 1,6-hexamethylene diisocyanate (HMDI)] were used. 2,4-Toluene diisocyanate [trademark Scuranate T100 (99% purity)] was acquired from Lyondell Basell (Netherlands), MDI (99% purity) from BASF (Germany), and HMDI from Sigma Aldrich (Belgium). Isocyanates were supplied in the ready-to-use form. All alcohols, with basic substance contents over 99%, were acquired from Alfa Aesar. Before synthesis, alcohols (butanol, isopropanol, etc.) were dried by means of freshly baked molecular sieves (4 Å).

To prepare the TPU, oligotetramethylene oxide diol with  $M_n = 1000 \text{ g}\cdot\text{mol}^{-1}$ , 4,4'-diphenylmethane diisocyanate (basic substance content  $\geq 99.5\%$ ) and 1,4-butanediol (basic substance content 99%, moisture concentration 0.1%) were used. Water contained in macrodiols, butanediol, and in the plasticizers was removed at a temperature of 90°C whilst stirring for 7 h at a residual pressure of 0.2 kPa.

TPU was prepared using a two-stage method. In the first stage, a prepolymer with end NCO groups was obtained. In the second stage, the prepolymer was cured using 1,4-butanediol.

Tributyl phosphate (TBP), dihexyl phthalate (DHP), dibutyl phthalate (DBP), and di(2-ethylhexyl) phthalate (DEHP) were used as suitable liquid plasticizers with low glass transition temperatures. The plasticizers were acquired from Sigma Aldrich.

To prepare high-density composites, microdispersive tungsten containing 18–22  $\mu\text{m}$  (ca. 70%) and 4–8  $\mu\text{m}$  fractions (ca. 30%) was used. Both fractions were supplied by the Kirovgrad Plant of Hard Alloys, Russia.

The preparative synthesis of diurethanes is set out in Ref. 34, which describes, in detail, the reaction for urethane formation in tetrahydrofuran in the presence of dibutyl tin dilaurate. This work also contains elemental analysis data of the obtained compounds. Synthesis of a large number of diurethane compounds conducted without the use of solvents in the presence of organo-tin compounds is described elsewhere.<sup>22,35</sup> The reaction between diisocyanates and alcohols is noted to proceed almost completely after 1–2 h at 70–80°C. However, as in our study, it is inexpedient, during synthesis of diurethanes, to use catalysts that are planned to be further applied as components in the polyurethane compositions, because admixtures of catalysts in the reaction mass decrease the technological properties appreciably.

The mechanism and kinetics of urethane formation are described elsewhere.<sup>2,36–38</sup> As the reaction progresses, the activity of the unreacted isocyanate groups significantly decreases and causes relative retardation of the reaction, especially at high degrees of conversion. At this point, the order of the reaction between diisocyanates and alcohols is assumed to be approximately equal to 2, provided that side reactions, in the absence of catalysis, do not occur. When arranging the synthesis of urethanes without catalysts at temperatures below 100°C, such reactions (formation of allophanate groups) may practically be neglected.<sup>36</sup>

During the preparation of diurethanes in this work, the method included a synthesis procedure that did not use solvents, provided that the finite melting temperature of the formed diurethane was below 80°C; otherwise, a solvent medium needed to be used. The laboratory equipment consisted of a three-neck glass flask equipped with stirrer, with a dropping funnel (or reflux cooler) and a thermometer. The flask was either cooled externally or heated in a water bath, depending on the temperature of the reaction mass. Alcohols were added to the diisocyanates in the flask using a dropping funnel. MDI was used as a 50% solution in butyl acetate. The ratio of the components needed for a 1% excess of alcohol (OH/NCO) was equal to

1.01. During the addition of alcohols to the reaction melt, the temperature in the flask was held at 60–80°C for 40–60 min, whereupon the reaction melt was additionally kept at 80°C for 2–3 h. The finished product was dried at 85–90°C for 2–3 h under vacuum in order to remove any residual alcohol. The optimal duration of the synthesis was determined by quantitatively analysing the free NCO groups in the reaction mass.

The synthesis of diurethanes with melting temperatures above 80°C was performed in a medium of octane or butyl acetate (50% of the initial reaction mix). Under these conditions, the temperature in the flask was held such that it did not exceed 60°C for 40–60 min (duration of dosing), and subsequently at 80°C (aging of the product). The finished product was washed with hexane and dried under vacuum at 50–60°C for 2–3 h. The completeness of conversion of the NCO groups was monitored with FTIR spectroscopy (adsorption band at wave number  $\nu = 2270 \text{ cm}^{-1}$ ) and titration using *n*-dibutylamine.

TPU specimens were synthesized in a two-stage process on the basis of oligotetramethylene oxide diol, MDI and butanediol. In the first stage, the interaction of MDI with oligotetramethylene oxide diol (at molar ratio of 2.5:1) produced a prepolymer. In the second stage, the prepolymer was cured with butanediol at molar ratios NCO/OH of either 0.95 or 0.98.<sup>39</sup> TPU prepared at NCO/OH = 0.95 was denoted TPU-1, and that at NCO/OH = 0.98 was denoted TPU-2. The completeness of conversion of the NCO groups was monitored with FTIR spectroscopy.

Polyurethane compositions were plasticized using two methods: (1) the plasticizer was directly added to the reaction mixture of prepolymer (based on oligotetramethylene oxide diol) and 1,4-butanediol, (2) by means of swelling the TPU, prepared without plasticizers, in melted plasticizer, up to a pre-set concentration value. Composites with high-dispersive tungsten (TPUW) were prepared by adding filler to the reaction mass plasticized during synthesis. Experiments were performed at two ratios of NCO/OH = 0.95 (TPUW-1) and 0.98 (TPUW-2). The reaction mass was produced under the same conditions described elsewhere.<sup>40</sup> The polyurethane binder contained 30 wt % plasticizer (BTU). The filled and unfilled TPU compositions were cured for 2 days at 80°C. The cured specimens were pressed in steel moulds at 120°C to form 2 mm-thick sheets. A part of the specimens was protractedly stored at temperatures below the melting point of the plasticizer. For comparison, not only diurethane plasticizers were tested, but also diphenyl phthalate (DPP,  $T_m = 73^\circ\text{C}$ ) and liquid plasticizers: DHP and TBP.

### Measurements

To determine density values of the plasticizers, specimens were hydrostatically weighted with the use of an analytical balance, AR-2140 (Ohaus), to  $3 \times 10^{-7} \text{ kg}$  accuracy. Melting points and glass transition temperatures were determined with a DSC 822e device (Mettler Toledo Star). To determine the melt-flow index (MFI) of the plasticized polyurethane compositions, a laboratory extrusion rheometer was used, in accordance with ASTM D1238. In view of the extremely high density of the filler used in the compositions ( $19.3 \text{ g/cm}^3$ ), the melt-index values for compositions containing different fractions of filler were recal-

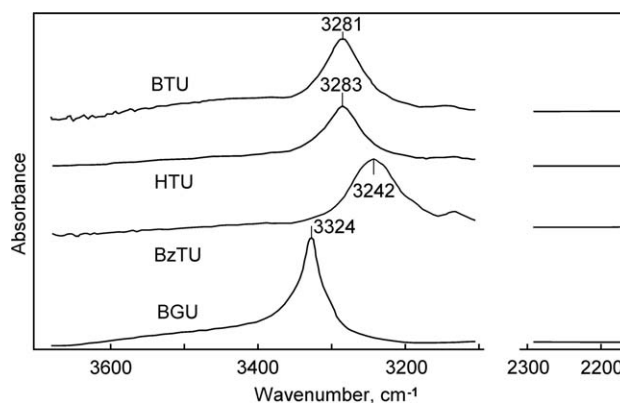


Figure 1. FTIR-spectra of some diurethanes.

culated in volume units. Viscosity values of the melted plasticizers were measured using a Heppler Rheometer viscometer.

Mechanical tests were performed with an Instron 3365 testing machine at a temperature of  $24 \pm 1^\circ\text{C}$ , and the stretching rate was  $0.28 \text{ s}^{-1}$ . The size of the samples used was  $2 \times 4 \times 30 \text{ mm}$ . Values were determined for the tensile strength  $\sigma_k$  (maximum stress calculated for the initial cross section of the sample) and relative critical strain  $\epsilon_k$ .

FTIR spectra were recorded using a Vertex 80v spectrometer, with spectral resolution of  $1 \text{ cm}^{-1}$ . Samples of TPU films with thicknesses of 10–15  $\mu\text{m}$  were prepared without volatile solvents, according to methods published elsewhere.<sup>40</sup> FTIR spectra of the pure diurethanes were recorded under ambient conditions by preparing the samples with KBr pellets. A background correction was performed using an identical blank KBr pellet. For convenient comparison, the spectral curves were normalized for the  $1600 \text{ cm}^{-1}$  band, which is typical for C–C valence vibrations of the aril ring.

Scanning electron microscopy images of the polyurethane samples were obtained using a scanning electron microscope (Evex HR-3000) at an accelerating voltage of 30 kV. Samples were used after 6 months storage at room temperature. To prepare specimens for experimental purposes, the low-temperature cleavage method was used. After that, specimens were plated with a conductive gold coating using a magnetron sputtering device (Quorum Q150T).

## DISCUSSION

### Physico-Chemical Properties of Plasticizers

A qualitative analysis of the FTIR spectra of fusible diurethane plasticizers shows the absence of a band at  $\nu \approx 2270 \text{ cm}^{-1}$ , indicating the completeness of conversion of the NCO groups. An intensive band of NH groups H-bonded with oxygen atoms in urethane groups is seen in the range of NH valence vibrations (Figure 1). The position of the band depends on the type of alcohol and diisocyanate used in the synthesis of the diurethane. The band of NH at  $\nu \approx 3242 \text{ cm}^{-1}$  shifts significantly to lower wave numbers towards the same band for BGU ( $\nu \approx 3324 \text{ cm}^{-1}$ ) on the base of aliphatic diisocyanate and aliphatic alcohol; this may be related to the enhanced close packing of aromatic molecules through  $\pi$ - $\pi$  interactions in BzTU. The positions of the peaks for bonded NH groups are close for BTU

**Table I.** Physico-Chemical Properties of Synthesized Diurethanes

		$\rho$ (kg/m <sup>3</sup> ) (25°C)	$T_m$ (°C)	$T_g$ (°C)	$\eta$ (Pa·s)(110°C)
1	R <sub>1</sub> -(NHCO-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> ( <b>BTU</b> )	1130	75-77	-13	0.46
2	R <sub>1</sub> -(NHCO-CH(CH <sub>3</sub> )-C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1092	87-89		0.19
3	R <sub>1</sub> -(NHCO-C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> ( <b>ATU</b> )	1075	93-95	-13	-
4	R <sub>1</sub> -(NHCO-C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub>	1077	77-79		-
5	R <sub>1</sub> -(NHCO-C <sub>7</sub> H <sub>15</sub> ) <sub>2</sub> ( <b>HTU</b> )	1027	76-78	-21	-
6	R <sub>1</sub> -(NHCO-(CH <sub>2</sub> ) <sub>3</sub> -CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub>	1074	73-75		-
7	R <sub>1</sub> -(NHCO-CH <sub>2</sub> -Ph) <sub>2</sub> ( <b>BzTU</b> )	1150	99-101	-2	0.23
8	R <sub>1</sub> -(NHCO-(CH <sub>2</sub> )-CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub>	1095	115-117		-
9	R <sub>1</sub> -(NHCO-CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub>	1137	133-136		-
10	R <sub>1</sub> -(NHCO-(CH <sub>2</sub> ) <sub>2</sub> -O-CH <sub>3</sub> )	1238	84-86		0.21
11	R <sub>1</sub> -(NHCO-(CH <sub>2</sub> ) <sub>2</sub> -O-C <sub>2</sub> H <sub>5</sub> )	1175	48-50		-
12	R <sub>2</sub> -(NHCO-CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub>	1114	150-152		0.34
13	R <sub>2</sub> -(NHCO-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	1121	113-115		-
14	R <sub>2</sub> -(NHCO-C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub>	1112	108-110		-
15	R <sub>2</sub> -(NHCO-(CH <sub>2</sub> ) <sub>3</sub> -CH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub>	1128	106-109		-
16	R <sub>2</sub> -(NHCO-(CH <sub>2</sub> ) <sub>2</sub> -O-C <sub>2</sub> H <sub>5</sub> ) ( <b>ETU</b> )	1204	89-91		0.31
17	R <sub>3</sub> -(NHCO-(CH <sub>2</sub> ) <sub>2</sub> -O-C <sub>2</sub> H <sub>5</sub> )	1119	66-68		0.25
18	R <sub>3</sub> -(NHCO-C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub>	1073	94-96		-
19	R <sub>3</sub> -(NHCO-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> ( <b>BGU</b> )	1035	88-90		-

R<sub>1</sub>—toluilen, R<sub>2</sub>—diphenylmethane, R<sub>3</sub>—hexamethylene.

and HTU (3281 and 3283 cm<sup>-1</sup>). The FTIR data permit us to suppose that the overwhelming majority of urethane groups in diurethanes are H-bonded. It is interesting to note the almost full agreement of the NH absorption peak position of BGU with the data given elsewhere.<sup>11</sup>

Values for the physico-chemical characteristics ascertained for the obtained diurethanes are summarized in Table I. It turned out that, while determining the thermic characteristics of the synthesized diurethane compounds, some diurethanes were only partially crystallized. Therefore, Table I includes not only the values of density ( $\rho$ ) and melting point ( $T_m$ ), but also glass transition temperature ( $T_g$ ), provided that the fusible plasticizers contain an amorphous fraction. Maximal deviation of the data, obtained by the differential scanning calorimetry (DSC) method, from average values, did not exceed 1.5%. For a number of diurethanes, the viscosity values of the melts were determined.

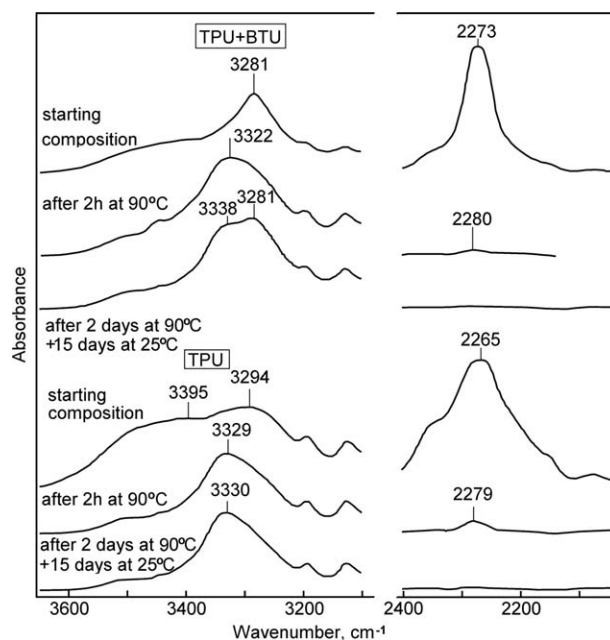
As is apparent from the obtained data, the melting temperature values for most of the synthesized plasticizers (predominantly of TDI-based) are below 100°C, and the viscosity values for the respective diurethane melts are moderate. Fusible diurethanes, namely, BTU, ETU, BzTU, HTU, and BGU, designated in Table I, were used for further investigations. For comparison, DBP and DPP plasticizers were also used. Diurethanes blended with liquid DHP and TBP plasticizers were also included in the test program to estimate the possibility of increasing frost-resistance.

### Structure and Properties of TPU and Highly Filled Composites with Fusible Compounds

FTIR spectra of TPU with and without diurethanes show a fast conversion of NCO groups (bands at 2273 or 2265 cm<sup>-1</sup>). After

the samples were kept for 2 days at 90°C and 15 days at 25°C, two absorption bands of bonded NH groups were seen (Figure 2).

The appearance of two NH bands in the FTIR spectrum of TPU with diurethane, where one coincided with BTU ( $\nu = 3281$  cm<sup>-1</sup>; Figure 1), indicates a phase segregation in the material. This suggestion was confirmed further by the DSC



**Figure 2.** Variations in FTIR spectra of polyurethane binders during the storage process.



**Table II.** Melt-Flow Index of Polyurethane Compositions with Various Plasticizers

Plasticizer	Initial polymer		Plasticization after synthesis		Plasticization at synthesis	
	TPU-1	TPU -2	TPU -1	TPU -2	TPU -1	TPU -2
BTU	0.01(2.4)	0(0.2)	1.3(12.1)	0.1(4.4)	95.2	9.6(84.4)
ETU			1.1(10.3)	0.1(4.2)	31.6	7.5(63.3)
DBP			0.9(8.8)	0 (2.2)	44.4	3.6 (21.2)
DPP			0.5(6.4)	0 (3.6)	30.2	1.7(17.6)

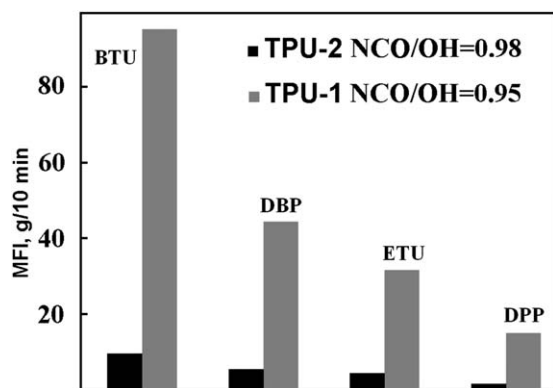
The value was determined at 120°C (the value at 140°C is given in parenthesis). The mass fraction of plasticizer is 30%.

data. The position of the other NH band ( $\nu = 3338 \text{ cm}^{-1}$ ) differs from that of TPU without plasticizer ( $\nu = 3330 \text{ cm}^{-1}$ ). It can be related to a partial dissolution of diurethane in the polyurethane matrix.

The technological properties of the polymer binder determine the possibility to process highly filled compositions. Incorporation of plasticizers enabled us to sharply reduce the viscosity value of the thermoplastic polyurethane binder.

As can be seen in Table II, 30% of the plasticizer added to the reaction mass during synthesis magnifies the melt-flow index at 120°C by over three orders of magnitude. However, plasticization of the already synthesized specimens results in only an approximate two-fold increase in the melt-flow index. Arguably, the availability of plasticizer in the reaction mass leads to the formation of shorter linear molecules of polyurethane. Such plasticized materials can be processed at temperature values 60–80°C lower than those with known nonplasticized TPU.<sup>41–43</sup> With these findings duly considered, further investigations were performed with TPU specimens that were plasticized during the synthesis.

Preliminary work evinced the use of an NCO/OH ratio beyond 0.95–0.98 during the synthesis of thermoplastic polyurethane to be inexpedient. The reason is that, in this case, the synthesis results in either low-strength specimens (at NCO/OH < 0.95), or specimens that cannot be processed at moderate temperatures (at NCO/OH > 0.98). The findings presented in Figure 3, for compositions plasticized with diurethanes and DPP, show that (a) technological properties are maximally improved with



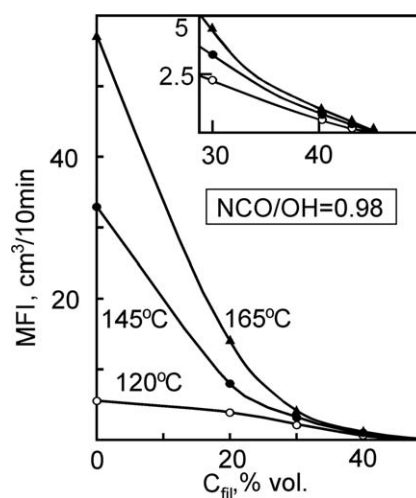
**Figure 3.** Melt-flow index of TPU at 120°C for a 30% fraction of plasticizer added at the synthesis stage.

the use of BTU as a plasticizer and (b) minimal improvement is observed with the use of DPP as a plasticizer without urethane groups. This effect is attributed to the significant decrease in inter-chain interactions in the polymer in the presence of an active plasticizer.<sup>44</sup>

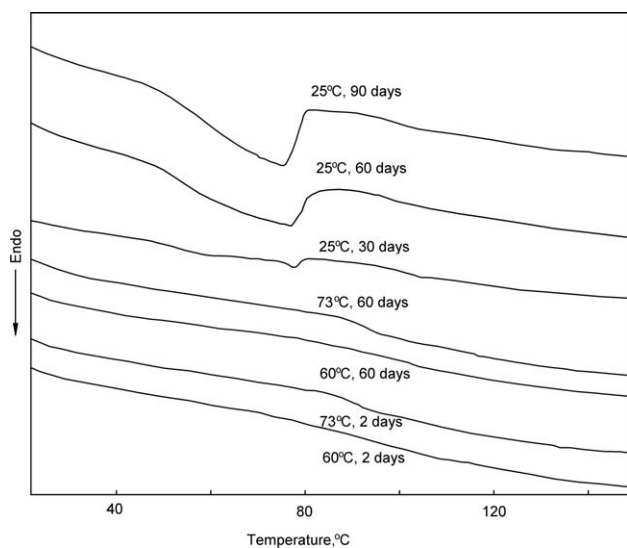
Figure 4 mirrors the melt-flow index versus filler-content dependence for a polyurethane composite containing micro-dispersive tungsten as the filler at 120–165°C. The composite contained 45 vol % tungsten filler, maximally. For MFI values under 1 cm<sup>3</sup>/10 min, specimens were produced using the blind pressing method.

Samples of TPU-1 plasticized with BTU were kept at different temperatures for 60–90 days. DSC data show a certain portion of the synthesized plasticizers introduced into the thermoplastic binder to be in a solid micro-dispersive phase, when stored below the melting point; this enables it to play a role of filler, which correlates with the above-mentioned spectral and DSC data.

The DSC curves in Figure 5 show the diurethane plasticizer BTU to be practically noncrystallized in the TPU specimens kept for 60 days at 60°C and 73°C, that is, close to the melting temperature of this diurethane (77°C). An endothermic effect, caused by the melting of the crystal phase, is observed after storage of specimens for 60 days at 25°C and for 90 days in 50–



**Figure 4.** Melt-flow index vs. tungsten filler content for thermoplastic composite TPUW-2 at different temperatures.



**Figure 5.** DSC curves of TPU-1 samples with BTU plasticizer (30 wt %) after storage at different temperatures.

75°C intervals. An analogous effect was observed for TPU with another diurethane plasticizer (ETU).

Crystallization positively influences the strength of TPU; this effect was observed for both TPU-1 and TPU-2 as well as filled TPUW-1 and TPUW-2 specimens with 94.3 wt % (or 43 vol %) tungsten (Figure 6).

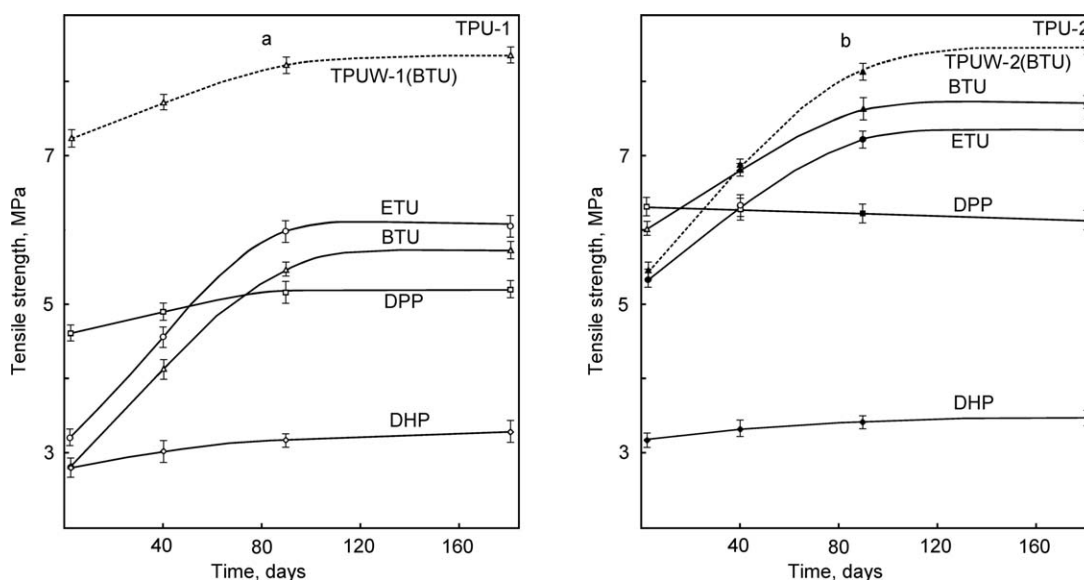
The engineering strength of TPU and TPUW specimens became almost constant after storage for 90 days at 25°C, which is approximately 1.5–2 times higher compared to that after storage for 2 days. The tensile strength of filled TPUW composites also increased appreciably. The engineering strength of polyurethane binder only varies slightly under same conditions when using liquid plasticizer DHP. The same effect relates to TPU-1 and TPU-2 specimens plasticized with fusible plasticizer DPP without urethane groups. This phenomenon is caused by intensive

crystallization of this plasticizer within several minutes at room temperature, unlike BTU or ETU.

The tensile strength value of polyurethane thermoplastics with DPP is lower compared to that of the elastomer with diurethane plasticizers. Availability of the crystalline phase in TPU with fusible plasticizers is confirmed by findings obtained with scanning electron microscopy. Particles have sizes of 2–3  $\mu\text{m}$  for DPP and 1–3  $\mu\text{m}$  for BTU (Figure 7). Particles of DPP are polyhedron-shaped, whereas 200–300 nm-thick flat particles prevail in BTU. Crystallization processes in BTU and ETU specimens are voluminal. Formation of H-bonds between diurethanes and the polyether matrix can be the reason for the TPU migration stability in diurethane applications. With regards to DPP, crystallization also proceeds on the surfaces of the specimens, thus being undesirable for practical uses of the material.

TPU-1 and TPU-2 specimens plasticized with 30% liquid plasticizer DHP are characterized by low strength. Soft polyurethane matrices plasticized with a polar plasticizer are typically observed to be weaker.

Comparison of failure stress values  $f_r = \sigma_k(\epsilon_k + 100)/100$  (true tensile strength) allows us to actually appraise the hardening effect of the binder, owing to crystallization of fusible plasticizers. The tensile strength values for TPU-1 and TPU-2 with diurethane plasticizers appreciably increased after storage for 90 days at 25°C, and the values were almost unchanged following storage. The true strength of the polyurethane binder specimens with diurethane plasticizers is (a) higher compared to that of the specimens with DPP and (b) significantly higher compared to that of specimens with liquid plasticizers. Furthermore, TPU-2 specimens, while under stress, manifest higher values of critical strain ( $\epsilon_k$ ). The true strength value of TPU-2 specimens determined at NCO/OH = 0.98 exceeds that of TPU-1 specimens synthesized at NCO/OH = 0.95. Conceivably, this phenomenon is attributed to the larger molecular mass of the polymer chains.

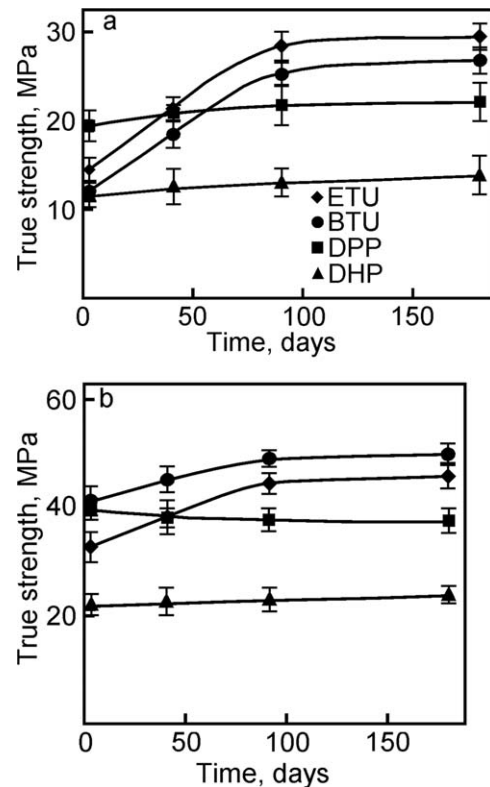


**Figure 6.** The tensile strength value vs. storage duration dependence for (a) TPU-1 specimens and (b) TPU-2 specimens at room temperature.

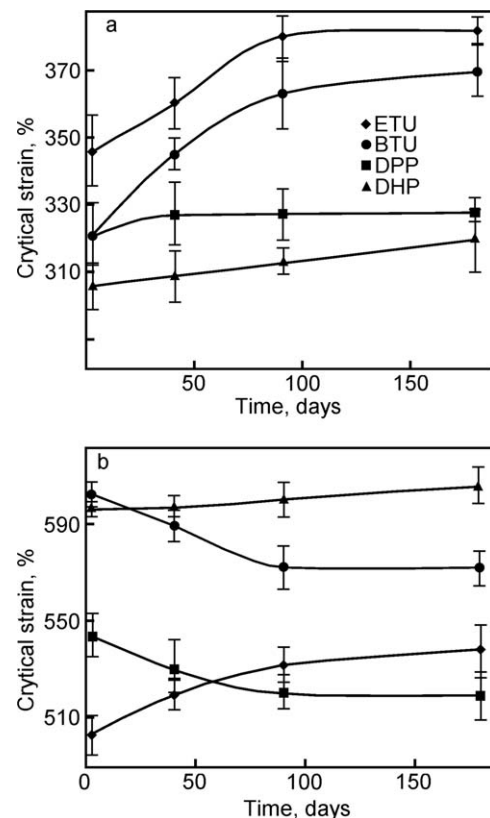


**Figure 7.** Scanning electron microscopy images of TPU-1 polyurethane specimens: (a) initial specimen without plasticizer, (b) specimen with 30% DPP, and (c) specimen with 30% BTU.

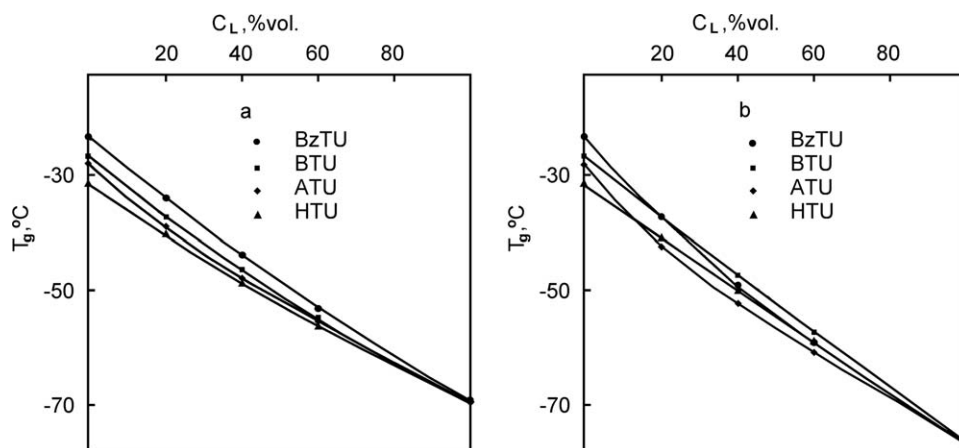
The engineering strength ( $\sigma_k$ ) of composites highly filled with tungsten (TPUW) is about 8 MPa (Figure 6) at relative critical strain  $\varepsilon_k = 42\text{--}44\%$ . This value is acceptable for practical purposes. However, such a high volume fraction of filler (43 vol %) does not lead to a hardening effect ( $f_r \approx 11$  MPa). This is attributed not only to defects in binder, but also to extensive local strains in stretched highly filled polymer systems. As a



**Figure 8.** Dependence of the true strength value of (a) TPU-1 and (b) TPU-2 specimens on the storage duration at 25°C.



**Figure 9.** Dependence of the critical strain value of (a) TPU-1 specimens and (b) TPU-2 specimens on the storage duration at 25°C.



**Figure 10.** Dependence of the glass transition temperature of TPU-1 samples vs. the content of low-molecular-mass liquid  $C_L$  in the mixture of plasticizers, consisting of diurethane and DHP (a) or TBP (b).

result, a composite will break at a lower macroscopic strain values, unlike a specimen of unfilled polymer.

To provide better rheological properties of TPU, the ratio of NCO/OH = 0.95 would be preferable. At this point, the physico-mechanical properties of composites with tungsten differ slightly from those of material produced at NCO/OH = 0.98 (TPUW-2). The revealed phenomenon may, presumably, be caused by interactions between end-capping hydroxyl groups in the TPU polymer and the surface of the filler. Low-toxicity highly filled thermoplastics of a new generation, with a density of  $9.4 \text{ g/cm}^3$ , can be used to protect various facilities from radioactive radiation, instead of using the highly toxic metal, lead.

#### The Effectiveness of the Application of Low-Molecular-Mass Liquids with Fusible Diurethanes in TPU Compositions

The use of low-molecular-mass liquids as plasticizers leads, as a rule, to a significant decrease in the glass transition temperature.<sup>44</sup> Upon addition of polar diurethanes with higher glass transition temperatures to TPU (Table I), the glass transition temperature of TPU varies with an opposing trend. This occurs because of the partial solubility of diurethane in the polymer matrix. A portion of plasticizer, as shown above, is in the crystalline state. The mentioned negative effect can be compensated by means of partial replacement of diurethane compounds by a liquid plasticizer with a low glass transition temperature, for example, DHP ( $T_g = -87^\circ\text{C}$ ) or TBP ( $T_g = -134^\circ\text{C}$ ). To corroborate this supposition, TPU synthesized with diurethane compounds BzTU, BTU, ATU, and HTU were tested.

The DSC data evidenced that the replacement of 30 vol % diurethane with liquid ester plasticizer (total content of plasticizer blend in compositions being 30%) permits a lower glass transition temperature by 20–25°C. At this point, the glass transition temperature of TPU attains a value of  $-50^\circ\text{C}$  (Figure 10), thus making polyurethane composites unusable under natural climate conditions.

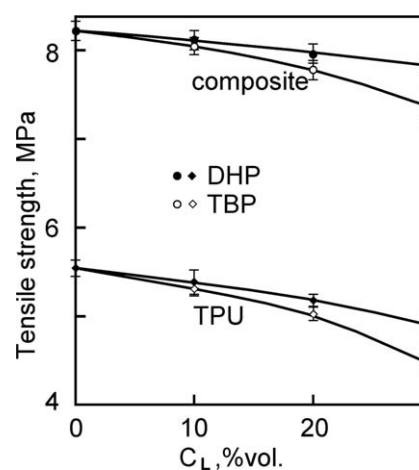
Upon partial replacement of diurethane with DHP (up to 30 vol %), the tensile strength of the tungsten-filled composite varies to a moderate extent (Figure 11).

The results of comprehensive studies of polyurethanes, plasticized by liquid and low-melt plasticizers, show a fruitful

approach for the development of a new type of thermoplastic material based on the use of fusible diurethanes (biscarbamates). A large number of diurethanes was synthesized to implement this approach; some of these compounds (with a low melting point) were successfully tested in filled and unfilled polymer systems with soft polyether and hard urethane segments.

The proposed direction of TPU development enables radically improved processing of highly filled polymer systems and the production of materials with acceptable physical and mechanical properties. Taking into account the data given elsewhere,<sup>8</sup> we can expect an increase in the thermal stability of a new type of TPU with diurethane compounds. Clear advantages of fusible diurethanes compared with other plasticizers determine the innovation attractiveness of TPU–diurethane systems.

A partial replacement of diurethanes by liquid plasticizers eliminates contradictions inherent to the "TPU–diurethane" system. A large amount of a plasticizer is needed to reduce the viscosity of the TPU, but the frost resistance of a material will decrease.



**Figure 11.** Dependence of the tensile strength of TPU samples vs. the content of liquid plasticizers  $C_L$  in the mixture with BTU. The ratio plasticizer: binder is equal to 30/70 in weight fractions. Samples were kept after preparation at  $25^\circ\text{C}$ ; duration time was 90 days.



Use of a mixed plasticizer can improve the frost resistance of TPU while a high strength is kept.

New types of binders with diurethanes offer new possibilities to develop various highly filled thermoplastics processed at low temperatures, which excludes the thermal degradation of the polymer matrix. These are examples of such possible TPUs, including high-density TPUs, TPUs with an energy dissipative filler to protection the action of shockwaves (pumice, porous metals), TPUs with magnetic properties and those that are conductive. The applicability of the synthesized diurethanes may be the subject of further studies, including biomedicine and agrochemical aspects.

## CONCLUSIONS

A series of low-molecular-mass aliphatic and aromatic diurethane compounds, with melting points below 100°C, was synthesized. These compounds are of interest as low-melting plasticizers for thermoplastic block-structured polyurethanes. The synthesis method of such compounds was proposed without using solvents. The introduction of low-melting urethane plasticizers to TUP with polytetramethylene soft segments was shown to reduce their processing temperature and to simultaneously increase the melt-flow index of the materials dramatically. It was stated that the significant hardening of both the diurethane-containing polymer binder and the composite containing a mineral filler (based on the mentioned polymer binder) after storage at 25°C was revealed to be caused by partial crystallization of diurethane. The crystalline phase under formation played a role as a reinforcing filler in TPU. Some diurethane is distributed in the polymer matrix; this is confirmed by DSC and FTIR spectroscopy data. It was shown that diurethanes combined with liquid ester plasticizers were ascertained to significantly improve the frost resistivity of polyurethane thermoplastics. At this point, the strength properties of TPU varied only moderately. As a result of these investigations, a new low-toxicity thermoplastic composite material was developed. It permits us to replace toxic lead completely, in all application areas, for radiation protection. The suggested approach can be used to design other polymer materials containing functional fillers.

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