Chapter 11

The Influence of the Size, Shape and Character of Nanofillers on Functional Properties of Polyurethane Elastomers

Milena Špírková, Rafał Poręba and Libuše Brožová
Institute of Macromolecular Chemistry AS CR, v.v.i., Prague, Czech Republic

Abstract

The chapter is aimed at polyurethane-inorganic nanofiller nanocomposite preparation and characterization. Polyurethane (PU) matrix is formed from aliphatic polycarbonate-based diol (MW ca. 2000; macrodiol, MD), hexamethylene diisocyanate (HDI) and butane 1,4-diol (BD; used as the chain extender). One-step procedure for PU and PU nanocomposite preparation was used. Equal ratio of MD-to-BD hydroxyl groups was used in the synthesis. PU and PU nanocomposites contain 81-82 wt. % of soft (polycarbonate-based) segments and 18 wt. % of hard segments (HDI-BD product). Pure PU matrix is distinguished by (i) thermoplastic character, (ii) high degree of the phase separation of soft and hard segments; (iii) low crystallinity (< 10%) and (iv) very good mechanical and thermomechanical properties, resulting from tensile tests and dynamic mechanical thermal analysis. Silica nanoparticles differing in size (7 to 40 nm) were used as the nanofiller in the concentration 1 wt. % in the PU nanocomposite. The influence of the size and character of the silica nanoparticles on the internal particle arrangement in PU matrix and on functional, e.g., mechanical, surface and barrier properties of PU nanocomposites was discussed, and compared with related nanocomposites containing layered nanoparticles (bentonite), studied previously.

Keywords: Nanocomposite; Polyurethane; Nanosilica; Microscopy; Mechanical and barrier properties

* Corresponding author address: Institute of Macromolecular Chemistry AS CR, Heyrovského nám. 2, 162 06 Praha 6, Czech Republic. Email: spirkova@imc.cas.cz.
1. Introduction

Polyurethanes (PUs) are very important synthetic polymers which can be utilized as flexible, semi-rigid or rigid materials prepared in the form of foams, elastomers or plastics. So far they have been mostly employed as construction and insulation materials (ca. 65% of PU production) in the form of foams (low-density, high-density and microcellular foams). PUs can be considered as randomly segmented copolymers composed of flexible soft segments and more rigid hard segments. Thermodynamic incompatibility of the soft and hard segments leads to the microphase separation, mostly on the sub-nanometer and nanometer scale. The broad practical use of segmented PUEs attracts a considerable attention of scientists and engineers. The up-to-date studies have been aimed mostly at the understanding the structure-property relationships.

Polyurethane elastomers (PUEs) are very important materials in spite of the fact that PUE production covers just ca. one eighth of PU market demand. PUE are thermoplastic materials which belong to the group of segmented copolymers. Thermoplastic materials are distinguished by the combinations of properties characteristics for plastic as well as for rubber materials. Unlike thermoset systems where the crosslinks are of strong covalent character, the crosslinking in thermoplastic systems is achieved via weaker dipole-dipole interaction or hydrogen bonds. The hydrogen bonds in PUEs can be relatively easily temporarily broken and then re-built, e.g., by increase/decrease of temperature. Hence, they can be processed as plastics at lower temperature and as viscous liquids at higher temperature. This phenomenon is very important, e.g., for PU recycling or reuse processes.

PUEs exhibit unique properties such as high strength, elongation at break, hardness, and good resistance to abrasion and to most aliphatic and aromatic liquids. They have been used as automotive panels, pneumatic tires, shoes, coatings, fibers, binder resins [1, 2], however they have been recently used in medical and biomedical applications [3-6]. Three basic components are used for PUE preparation: oligomeric diol containing primary or secondary hydroxyl groups (macrodiol), isocyanate component (diisocyanate or polyisocyanate of aromatic, cycloaliphatic or aliphatic character) and the chain extender (“short” diol or diamine). Classical macrodiols based on oligomeric polyethers on polyesters have been used in a number of recipes, but nowadays polycarbonate-based polyurethanes are more and more prepared and studied [7-27]. Two basic procedures (one-step or two-step, i.e., prepolymerization technique) are used for PUE preparation. From the technological point of view, it is important that very different PUE products can be prepared from the very same reaction mixture just by changing the reaction conditions (temperature, time, solvent, catalyst). The addition of nanofillers of different size and shape (nanosilica, clay, nanotube, graphene, POSS, cellulose nanocrystal, etc.) at low concentration (mostly units of wt. %) represents other way of modification of PUE functional properties [28-40].

Due to good mechanical properties and good blood compatibility, the modified PUEs are currently used as advanced biocompatible materials with specialty functions. Two basic strategies of biomedical application of PUs exist: The first one assumes the synthesis and use of PUEs with improved biostability (utilized as long-term implanted devices, cardiovascular applications, vascular prostheses, catheters, and prosthetic valve leaflets etc.) [19, 21, 41-43]. The second strategy is aimed at biodegradable PUEs materials (used in controlled drug delivery systems, as cardiovascular grafts) but they also can be used as temporary scaffolds in
tissue engineering for easier tissue regeneration [3, 44-46]. Artificial scaffolds used in tissue engineering and regenerative medicine should have mechanical properties resembling those of the healthy target tissue in order to avoid or minimize unwanted inflammatory reactions. Elastic moduli of natural tissues vary in several orders of magnitude, from units of kPa (e.g., in brain) to units of MPa (in bone tissues). From this point of view, a broad choice of suitable polymer elastomers with different mechanical properties is desirable to cover all individual tissue regeneration treatments. Development of proper synthetic biodegradable materials with appropriate mechanical and targeted functional properties (e.g., suitable biocompatibility, non-toxicity, high surface area, tailored degradation speed from weeks to years) is the focal point of biomaterial science, especially in the last decade [3-6, 19-21, 32, 33, 39, 41-45, 47-51]. Even though numerous polymer materials were synthesized and tested for this purpose [51], segmented polyurethanes (PUs) and polyurethane ureas (PUUs) were found as one of the most prosperous kind of biomaterials reaching abovementioned properties [3-6, 42-51].

Recently, we have prepared and characterized a series of all-aliphatic polycarbonate-based PU and PU nanocomposite elastomers containing small amount of layered nanoparticles (modified montmorillonite and bentonite) [22-27, 52, 53]. Macrodilis of different chain constitution (T5652, T4672 and T4692) and length (MW ca. 1000 and 2000) were tested. The influence of the concentration of hydrophilic silica nanoparticles on static and dynamic mechanical properties of T5652-based PU nanocomposites was studied as well [26]. This chapter is the extension of our current research in the field of nanocomposites based on polycarbonate-based PU matrix made from T4672 macrodiol. As nanoadditives, hydrophilic or hydrophobic fumed silica nanoparticles were used. The influence of the size and character of the silica nanoparticles on the internal particle arrangement and on functional, e.g., mechanical, surface and barrier properties of PU nanocomposites was discussed, and compared with related nanocomposites containing layered nanoparticles (bentonite) studied previously [52, 53]. The potential application use of polyurethane nanocomposites as biomaterials is expected (elastic and simultaneously tough coatings or films).

2. Methods

2.1. Experimental

The aliphatic polycarbonate diol with the number average of molecular weight ca 2000, T4672 (macrodiol, MD), provided kindly by Asahi Kasei Chemical Corporation was used as the source of flexible, soft segment PU part. MD was prepared by random copolymerization of butanediol and hexanediol with ethylene carbonate. The currently used nomenclature is the following: first two numbers are numbers of methylene units in the copolymer (C4 and C6), the third is the molar ratio of the tetramethylene units, and the last number indicates the molecular weight of PC diol (in thousands) [8]. (The characteristics of T4672 macrodiol have been given by the supplier: OH value: 54.2 mg KOH/g, water content 0.0077 wt.%, viscosity at 50°C: 18300 mPa·s). Hexamethylene diisocyanate (HDI), butane-1,4-diol (BD) (source of hard segment domains) and catalyst dibutyltin dilaurate (DBTDL), were supplied by Fluka. Three nanofillers based on fumed silica differing in size and surface character were used: “NanoSilica Powder Grade 999” from Elkem Silicon Materials, “AEROSIL® R 974” and
“AEROSIL® 380” both from Evonik Industries AG. (Their specification and codes are given in Table 1a). The silica nanoparticles differ in the surface character, which is either hydrophilic (untreated surface, A7 and N40) or hydrophobic (dimethyldichlorosilane-treated surface, A12). Due to the fact that all particles are very small, they have high surface-to-volume ratio. Hence, the surface character (modification) of the particle plays a significant role for the whole particle. For short, we use in the book chapter the term "hydrophilic/hydrophobic character of nanoparticles" instead of “hydrophilic/hydrophobic character of the surface of nanoparticles, controlled by their chemical modification”.

All samples were prepared in the form of films using a one-step procedure with constant ratios of functional groups [NCO]/[OH] = 1.05 and [OH]MD/[OH]BD = 1. The catalyst concentration was 50 ppm. The preparation schema is shown in Figure 1. The homogeneous dispersion of the nanofiller (1 wt. % in all cases) was achieved by one day swelling in macrodiol and butanediol mixture and a brief mixing before addition of catalyst and disiocyanate. After degassing, the mixture was poured into Petri dish and kept in nitrogen atmosphere at 90°C for 24 h. The final thickness of PU films was 0.3 ± 0.05 mm. The characteristics of PU and PU nanocomposites is given in Table 1b.

![Figure 1. Schema of PU and PU nanocomposite preparation.](image)

### Table 1. Characteristics of nanofillers (a) and of polyurethane and polyurethane nanocomposites (b)

#### (a)

<table>
<thead>
<tr>
<th>Silica nanoparticles</th>
<th>Code</th>
<th>Particle size, nm</th>
<th>Specific surface area, m²/g (BET)</th>
<th>SiO₂ content</th>
<th>Surface character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosil® 380</td>
<td>A7</td>
<td>7</td>
<td>380 ± 30</td>
<td>&gt; 99.8</td>
<td>hydrophilic</td>
</tr>
<tr>
<td>Aerosil® R974</td>
<td>A12</td>
<td>12</td>
<td>170 ± 20</td>
<td>&gt; 99.8</td>
<td>hydrophobic*</td>
</tr>
<tr>
<td>NanoSilica® 999</td>
<td>N40</td>
<td>40</td>
<td>50 ± 10</td>
<td>&gt; 99.98</td>
<td>hydrophilic</td>
</tr>
</tbody>
</table>

* hydrophobic fumed silica after treated with dimethyldichlorosilane.

#### (b)

<table>
<thead>
<tr>
<th>Code</th>
<th>Nanofiller</th>
<th>Hard segment contents (%)</th>
<th>Degree of crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-0</td>
<td>None</td>
<td>17.8</td>
<td>7.1</td>
</tr>
<tr>
<td>PU-A7-HI</td>
<td>A7</td>
<td>17.7</td>
<td>8.8</td>
</tr>
<tr>
<td>PU-A12-HO</td>
<td>A12</td>
<td>17.4</td>
<td>9.3</td>
</tr>
<tr>
<td>PU-N40-HI</td>
<td>N40</td>
<td>17.6</td>
<td>11.0</td>
</tr>
</tbody>
</table>

2.2. Transmission Electron Microscopy (TEM)
Ultrathin sections of the films were cut at low temperature (sample temperature – 80 °C, knife temperature – 50 °C) using an ultramicromtome with cryo attachment (Ultracut UCT; Leica). The sections were transferred to supporting Cu grids and observed using a transmission electron microscope (TEM; Tecnai G2 Spirit; FEI). The TEM micrographs were taken in bright field imaging mode at 120 kV; under these conditions, the micrographs showed darker crystalline aggregates and dark particles in the lighter polymer matrix.

2.3. Wide-angle X-ray Diffraction (WAXD)

Diffraction patterns were obtained using a powder diffractometer HZG/4A (Seifert GmbH, Germany) in reflection mode. The radiation CuKα (wavelength λ=1.54 Å, 40 kV, 45 mA) monochromatized with Ni foil (β filter) was used. The measurement was done in range 2θ = 1.4 – 40° with step 0.1°, where 2θ is the scattering angle. Exposure time at each step was 10 seconds. The degrees of crystallinity Cr were calculated with help of integral intensities diffracted by crystalline C and amorphous A part of materials according to relation Cr = C/(C + A).

2.4. Atomic Force Microscopy (AFM)

Investigation of the topography and heterogeneity relief of the PU and PU nanocomposite film surfaces was done by the atomic force microscope (Dimension Icon, Bruker), equipped with the SSS-NCL probe, Super Sharp SiliconTM - SPM-Sensor (NanoSensorsTM Switzerland; spring constant 35 Nm⁻¹, resonant frequency ≈ 170 kHz). Measurements were performed under ambient conditions using the tapping mode AFM technique. The scans covered the sizes from 1 x 1 to 50 x 50 μm².

2.5. Tensile Characterization

Static mechanical properties were measured on an Instron model 5800 (Instron Limited, UK) at 23°C by ISO 527 method. Dumbbell shaped specimens (type ISO 527-2/5B; total specimen length 35 mm, length and width of the narrowed part: 12 and 2 mm, thickness 0.3 mm) and test speed 0.167 mm.s⁻¹ were used for the analysis. The reported values are averages obtained from at least five specimens.

2.6. Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis was carried out on ARES-G2 from Rheometrics Scientific (now TA instruments) using an oscillation frequency of 1 Hz, deformation ranging automatically from 0.01% (glassy state) to 3.5% (maximum deformation allowed), over a temperature range of –100 to 180 °C, at a heating rate of 3 °C.min⁻¹. Dynamic torsion measurements were performed using rectangular samples, to which a constant tension force
of 5 g was applied. The standard specimen dimensions were 25 x 6 x 0.3 mm$^3$. Storage modulus ($G'$), loss modulus ($G''$) and loss factor ($\tan \delta$, $\tan \delta = G''/G'$) were measured. In this work, the glass transition temperature was defined as the temperature of maximum value of $\tan \delta$, ($\tan \delta)_{\text{max}}$.

2.7. Gas Transport Properties (GTP)

Gas transport properties of samples prepared in the form of free-standing self-supporting films were determined using a laboratory high-vacuum apparatus with a static permeation cell [54]. After a high vacuum was reached in the apparatus, the studied gas under constant pressure $p_i$ higher than atmospheric was brought into the feed part of the apparatus. Permeability was determined from the increase in pressure $\Delta p_p$ in calibrated volume $V_p$ of the product part per the time interval $\Delta t$ and was calculated using the formula

$$ P = \frac{\Delta p_p}{\Delta t} \cdot \frac{V_p}{s} \cdot \frac{l}{R T} $$

(1)

where $l$ is film thickness, $s$ is film area, $T$ is temperature and $R$ is the gas constant. All measurements were carried out at 30 °C.

Gas transport properties were studied for oxygen, nitrogen, carbon dioxide, methane and hydrogen. Their purity was higher than 99.95%.

The permeation of gas molecules through flawless polymer films occurs by the steps of solution of a permeant in the polymer and diffusion of the dissolved permeant. The permeability ($P$) is the product of the diffusion coefficient ($D$) and the solubility coefficient ($S$) and the solubility coefficient can be expressed as

$$ S = \frac{P}{D} $$

(2)

The diffusion coefficient was calculated from time lag ($\Theta$) and the film thickness ($l$) according to the equation (3).

$$ D = \frac{l^2}{6\Theta} $$

(3)

3. Results and Discussion

In this chapter, all-aliphatic polycarbonate-based polyurethane elastomer (PU-0) and three nanocomposites with nanosilica particles were synthesized in one-step-procedure.
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Figure 2. Possible H-bonds in urethane-carbonate groups (a), and in urethane units (b, c).

As all components are bifunctional, linear PU chains are composed of alternating elastic soft segments (SS) originating from the aliphatic polycarbonate diol component (macrodiol, with MW ca. 2000), and more rigid polar hard segments (HS) formed by HDI/BD building units which have the tendency for ordering to hard segment domains (HSD) and form semicrystalline structures. Hard segments arising from diisocyanate and chain extender feature the formation of a strong physical network by H-bonding among –NH and –C=O groups in urethane (-NHCOO-) units resulting in material reinforcement. Moreover, in our case, (secondary) H-bonding via –NH groups of urethane units and carbonate carbonyl groups of macrodiol (hard-soft segment H-bonds) comes into account, because T4672 contain regularly distributed carbonate (O-C=O) groups in the chain. Possible hydrogen bonded structural motives are given in Figure 2.

3.1. Transmission Electron Microscopy

The internal arrangement of PC-PU matrix itself and the distribution of silica nanoparticles in PC-PU nanocomposites were studied by TEM. Results are shown in the Figure 3. Spherulites (the result of HS ordering) of size 2-3 µm were detected both in PC-PU matrix and in all PC-PU nanocomposites. Silica nanoparticles are present in the form of agglomerates in all nanocomposites; they are regularly distributed both in soft-rich and hard-rich part of PC-PU nanocomposites. The size of agglomerates decreases with increasing average size of the nanoparticles. While the smaller A7 and A12 nanoparticles are present as chain-like formations of size about 1 µm, the bigger N40 nanoparticles form just small spherical agglomerates (< 0.5 µm). In summary, TEM micrographs suggest that the average particle size controls the nanoparticle arrangement in PC-PU nanocomposites. On the other hand, the hydrophilic/hydrophobic character of silica does not have an observable impact on the internal particle ordering.

3.2. Wide-angle X-ray Diffraction

PU matrix and PU nanocomposites were analyzed by WAXD for gaining more information on the nanofiller influence on the internal arrangement (mainly crystallinity) of the systems. It was found that all samples are partially crystalline.
Figure 3. TEM images of PC-PU matrix (a), and PC-PU nanocomposites containing 1 wt. % of hydrophilic nanosilica A7 (b), N40 (d) and hydrophobic A12 nanoparticles (c). (Spherullite structures are highlighted by squares).
The crystallinity is slightly higher in all nanocomposites (9 to 11 %) as compared with the crystallinity of the pure PU matrix (7 %). This finding is in accordance with scattering experiments of bentonite-containing PU nanocomposites [53]. The crystallinity in PU nanocomposites slightly increases with particle size: the crystallinity fraction in nanocomposites containing both smaller (A7 and A12) nanofillers is ca. 9 %, while the degree of crystallinity of nanocomposite with bigger N40 nanoparticles is 11 %. For further details, see Table 1b, Figure 4 and Ref. [53]. The slight difference in crystallinity of PU nanocomposites can be attributed to different arrangements of nanoparticles in PU matrix, as detected by TEM (Figure 3). The hydrophilic or hydrophobic character of silica nanoparticles does not practically influence the degree of crystallinity, however.

3.3. Atomic Force Microscopy

Surface morphology and heterogeneity were tested on all prepared films. Figure 5 shows 3D images of 50 x 50 µm² sample surfaces. Pure PU matrix and nanocomposite PU-N40-HI have very similar reliefs; the nanocomposite PU-A7-HI has the roughest surface relief. 2D height and phase images of film surfaces (size 5 x 5 µm²) are depicted in Figure 6. It is well visible that pure PU matrix has the smoothest surface and is the most homogeneous (phase difference in units of degree). All nanocomposite films have rough reliefs caused by the nanofiller presence. Roughness values are summarized in Table 2. From Figure 5 and 6 and Table 2 follows, that nanofiller size is the factor controlling the roughness and heterogeneity degree; both factors decrease with increasing size of silica particles. Film PU-N40-HI (with particles ca. 40 nm) has AFM characteristics very similar to unfilled PU film (PU-0). Nanofiller character (hydrophilic/hydrophobic) has no pronounced influence on the abovementioned characteristics, however.

![Figure 4. WAXD patterns of PU matrix and PU nanocomposites. For sample codes, see Table 1b.](image-url)
Table 2. Surface roughness of PU and PU nanocomposite films

<table>
<thead>
<tr>
<th>Code</th>
<th>Surface area (μm²)</th>
<th>$R_q$ (nm)</th>
<th>$R_a$ (nm)</th>
<th>$R_{max}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-0</td>
<td>25.1</td>
<td>18</td>
<td>14</td>
<td>152</td>
</tr>
<tr>
<td>PU-A7-HI</td>
<td>26.6</td>
<td>87</td>
<td>70</td>
<td>618</td>
</tr>
<tr>
<td>PU-A12-HO</td>
<td>25.4</td>
<td>44</td>
<td>36</td>
<td>233</td>
</tr>
<tr>
<td>PU-N40-HI</td>
<td>25.2</td>
<td>19</td>
<td>15</td>
<td>166</td>
</tr>
</tbody>
</table>

Surface area: the total area of examined sample surface (the three-dimensioned area of a given region expressed as the sum of the area of all the triangles formed by three adjacent data points).

$R_q$ (Rms): the standard deviation of the Z values within the given area.

$R_a$ (mean roughness): the mean value of the surface relative to the center place.

$R_{max}$ (max height): the difference in height between the highest and lowest points on the surface relative to the mean plane.

Mean: the average of all Z values within the enclosed area.

3.4. Tensile Properties

Tensile properties of PU-0 and PU nanocomposites (PU-A7-HI, PU-A12-HO and PU-N40-HI) have been investigated. The influence of the size and character of silica
nanoparticles on tensile strength, elongation at break, Young, M100 and M300 moduli and on toughness was evaluated. The results are given in Table 3 and Figure 7.

Figure 6. Height images (left) and phase images (right) of films PU-0 (a), PU-A7-HI (b), PU-A12-HO (c) and PU-N40-HI (d). (Images are of size 5 x 5 µm², black-and white scale is 500 nm for height and 50 deg for phase images).
### Table 3. Tensile properties of PU matrix and PU nanocomposites

<table>
<thead>
<tr>
<th>Code</th>
<th>Stress at break (MPa)</th>
<th>Strain at break (%)</th>
<th>Modulus Young’s (0.5-5%) (MPa)</th>
<th>Modulus 100% (MPa)</th>
<th>Modulus 300% (MPa)</th>
<th>Toughness (mJ∙mm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-0</td>
<td>57.1 ± 5.6</td>
<td>691 ± 24</td>
<td>56.8 ± 1.3</td>
<td>7.1 ± 0.1</td>
<td>15.3 ± 0.2</td>
<td>146 ± 13</td>
</tr>
<tr>
<td>PU-N40-HI</td>
<td>45.7 ± 7.4</td>
<td>652 ± 39</td>
<td>56.9 ± 2.8</td>
<td>6.7 ± 0.2</td>
<td>14.8 ± 0.8</td>
<td>121 ± 19</td>
</tr>
<tr>
<td>PU-A7-HI</td>
<td>31.6 ± 3.4</td>
<td>794 ± 44</td>
<td>45.2 ± 1.0</td>
<td>4.9 ± 0.1</td>
<td>9.6 ± 0.4</td>
<td>110 ± 11</td>
</tr>
<tr>
<td>PU-A12-HO</td>
<td>64.7 ± 2.7</td>
<td>908 ± 35</td>
<td>53.1 ± 2.6</td>
<td>6.0 ± 0.1</td>
<td>12.1 ± 0.2</td>
<td>210 ± 11</td>
</tr>
<tr>
<td>4672/1/0/18b</td>
<td>53.4</td>
<td>992</td>
<td>34.1</td>
<td>7.0</td>
<td>11.7</td>
<td>216</td>
</tr>
</tbody>
</table>

*Toughness is expressed as the energy necessary to break the sample per volume unit.

*b Data available in Ref. [53], Table IV.*

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**Figure 7.** Stress-strain dependences for PU matrix and PU nanocomposites. For sample codes, see Table 1b.

In contrast to the morphology (studied by AFM microscopy), the hydrophobic/hydrophilic character of the nanofiller has a dominant effect on tensile properties. All stress-strain curves are characterized by S-shape form indicating the strain-induced crystallization. The stress-strain curves of PU and PU nanocomposites have been described in detail in our previous paper [25]. The least pronounced S-shape is observed for the sample PU-A7-HI. The stress-strain dependence of nanocomposite PU-N40-HI containing hydrophilic 40 nm particles resembles the curve of pure matrix, PU-0 (Figure 7). However, the presence of nanoparticles in PU-N40-HI is apparently responsible for earlier break in the region of distinct strain-induced crystallization (over 600% elongation). This results in reduction of the elongation-at-break by 6% and tensile strength by 20%, if compared results of PU-N40-HI with PU-0. The presence of smaller particles A7 and A12 influences substantially the stress-strain dependences: the moduli (Young, M100 and M300) are lower as compared with the pure PU-0 matrix. The higher is the elongation, the bigger differences in stress for individual samples exist. (For example, tensile stresses necessary to achieve 600% of elongation are 38.5 MPa for PU-0, 36.7 MPa for PU-N40-HI, 25.8 MPa for PU-A12-HO and 18.7 MPa for PU-A7-HI). Toughness values decrease in order PU-A12-HO > PU-0 > PU-N40-HI > PU-A7-HI. The toughness (expressed as the energy per unit volume necessary to break the sample) can
be taken as a certain quality criterion. We can conclude that a significant improvement of tensile properties (compared to pure matrix) at 1 wt. % load can be achieved only by addition of hydrophobic nanosilica. If hydrophilic nanosilica particles are used, the large particles (40 nm) have almost no influence on tensile properties. The smaller (7 nm) particles deteriorate considerably tensile strength and toughness as compared to unfilled matrix (PU-0).

According to our experience, tensile characteristics for a given PU composition depend not only on the preparation procedure, but also on the shape of tested material (length and width, but especially sample thickness) and on conditions of testing (test speed). Therefore, the comparison of tensile properties can be done only for materials with all the above mentioned parameters identical. Otherwise, the test has only a qualitative character. Our previous study on a very similar PU material [25] revealed that almost identical toughness is obtained if sheets (thickness 2 mm) and films (0.5 mm) were tested. The sheets had somewhat higher tensile strength and lower elongation at break than the films. However, the differences (decrease in toughness compared to sheets) were observed for thinner films (200 - 300 µm). The thinner is the sample; the higher probability exists that a small defect can lead to noticeable deterioration of ultimate mechanical properties. The film PU-0 can be qualitatively compared with our previously studied sample 4672/1/0/18 [53]. PU-0 and 4672/1/0/18 have identical composition and conditions of sample preparation, but they differ in the thickness (2 mm for 4672/1/0/18 vs. 300 µm for PU-0). Also tensile testing conditions (especially sample shape) are different. Tensile characteristics of 4672/1/0/18 are given in Table 3, last line. Toughness of PU-0 is about 70 % of 4672/1/0/18 value. However, the film PU-A12-HO has almost the same toughness as 4672/1/0/18. In this way, hydrophobic A12 is very promising nanofiller for PU matrix and PU-A12-HO is very auspicious material for potential practical use as the highly elastic and tough coating.

3.5. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA analysis has been used to study the phase transitions (e.g., $T_g$ and $\beta$ relaxation of soft segments, $T_m$ of hard segment domains) in the PU matrix and in PU nanocomposites. The effect of the size and character of nanosilica additives on the dynamic mechanical properties of the nanocomposites was tested as well. Dependences of the storage modulus $G'$ and the loss factor tan $\delta$ as function of temperature are displayed in Figure 8 for all tested samples. The $G'$ vs. temperature and tan $\delta$ vs. temperature dependences show a glass transition near $T_g = –30 ^\circ$C, associated with the polycarbonate-based soft segments. The peak does not change the position with addition of different nanosilica particles. Similar results were obtained if layered silicates (bentonite for organic systems in concentration 1 and 2 wt. %) were added into PU matrix [53]. No change $\Delta T_g$ between pure PU matrix and composites indicates that presence of silica nanoparticles does not significantly influence flexibility of polycarbonate soft segments and that all silica particles interact preferably with hard segments.

For the second transition observed at approx. 50 $^\circ$C, a full and unambiguous interpretation has not yet been offered. Several hypotheses have been proposed: transition between 50 and 80 $^\circ$C was assigned to the disruption of short-range HS ordering [55,56], melting of HS domains [8], breaking up of the less ordered noncrystalline hard-segment domains [16], short-range ordering of hard segment domains as a result of the annealing and quenching
[57], hard-segment disordering in the boundary region between soft and hard phases [58], the relaxation of chain segments in the diffused interface between soft and hard segment domains [24, 59] or to transitions in domains of soft segments especially if contents of soft segment is high [16] (as in our case). Last but not least, the existence of a diffused interfacial region between SS and HS has been deduced from the order-disorder relaxation of the PU chain segments in the interface [59] and melting of noncrystalline hard-segment domains [8] in the interfacial region has been also suggested. The least pronounced step for PU-A12-HO is probably due to strengthening of the physical network by increasing the number of physical crosslinks between H-H segments. DMTA results are consistent with those obtained from mechanical tensile properties tests. The most noticeable $G'$ decrease was observed for PU-A7-HI that also showed the worst tensile mechanical properties. It seems that A7 silica weakened hard segment interactions. This phenomenon leads to the decrease of storage shear modulus after this transition (and finalizing in the lowering the melting temperature of the sample). Presence of small A7 particles probably restricts the number of hydrogen bonds which hinders the formation of strong H-H segment interactions.

Figure 8. Temperature dependences of the storage shear modulus $G'$ (top) and tan $\delta$ (bottom). For sample composition, see Table 1b.
3.6. Gas Transport Properties

The presence of nanosize admixtures in thin films and coatings can significantly influence gas transport properties of thin polymeric layers. Recently we have tested the influence of HS content, of the constitution of polycarbonate chain and of the presence/absence of bentonite in polycarbonate-based polyurethane elastomers [53]. In this contribution, we have studied the effect of the size and character of nanosilica filler on gas transport properties for polyurethane matrix and for three PC-PU nanocomposites. Permeability (a), diffusion coefficient (b), solubility (c) and selectivity (d)

<table>
<thead>
<tr>
<th>Code</th>
<th>Permeability $10^{16}$ (mol cm$^{-1}$ s$^{-1}$ Pa$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>CH$_4$    N$_2$    O$_2$    CO$_2$    H$_2$</td>
</tr>
<tr>
<td>PU-0</td>
<td>5.35      2.32      7.81      87.4      28.2</td>
</tr>
<tr>
<td>PU-N40-HI</td>
<td>5.43      2.20      7.11      84.4      26.6</td>
</tr>
<tr>
<td>PU-A7-HI</td>
<td>4.71      1.86      6.20      73.7      21.0</td>
</tr>
<tr>
<td>PU-A12-HO</td>
<td>5.39      2.34      7.16      87.0      27.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Code</th>
<th>Diffusion coefficient $10^{11}$ (m$^2$ s$^{-1}$)</th>
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<tbody>
<tr>
<td></td>
<td>CH$_4$    N$_2$    O$_2$    CO$_2$    H$_2$</td>
</tr>
<tr>
<td>PU-0</td>
<td>1.26      1.97      4.17      1.47      36.5</td>
</tr>
<tr>
<td>PU-N40-HI</td>
<td>1.26      1.86      3.85      1.54      16.8</td>
</tr>
<tr>
<td>PU-A7-HI</td>
<td>0.97      1.43      2.52      1.24      8.97</td>
</tr>
<tr>
<td>PU-A12-HO</td>
<td>1.08      2.07      3.18      1.48      58.6</td>
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<table>
<thead>
<tr>
<th>Code</th>
<th>Solubility $10^5$ (mol m$^{-3}$ Pa$^{-1}$)</th>
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<tr>
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<td>CH$_4$    N$_2$    O$_2$    CO$_2$    H$_2$</td>
</tr>
<tr>
<td>PU-0</td>
<td>4.24      1.18      1.88      59.6      0.77</td>
</tr>
<tr>
<td>PU-N40-HI</td>
<td>4.32      1.18      1.98      54.7      1.59</td>
</tr>
<tr>
<td>PU-A7-HI</td>
<td>5.19      1.31      2.45      59.6      2.34</td>
</tr>
<tr>
<td>PU-A12-HO</td>
<td>4.99      1.31      2.25      58.6      0.82</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Code</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O$_2$/N$_2$</td>
</tr>
<tr>
<td>PU-0</td>
<td>3.36</td>
</tr>
<tr>
<td>PU-N40-HI</td>
<td>3.23</td>
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<tr>
<td>PU-A7-HI</td>
<td>3.32</td>
</tr>
<tr>
<td>PU-A12-HO</td>
<td>3.06</td>
</tr>
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</table>

The final sample softening, during which all physical crosslinks disrupt and the sample starts to behave as a typical polymer melt, takes place in the range between 100 and 150 °C in all cases. The system containing small hydrophilic silica particles, PU-A7-HI has the lowest softening temperature, while PU-A12-HO shows the highest thermal stability (Figure 8).
transport properties. Permeability \((P)\), diffusion coefficient, \((D)\), solubility \((S)\) and selectivity for industrially interested gas (\(N_2\), \(O_2\), \(H_2\), \(CH_4\) and \(CO_2\)) were evaluated. The results are summarized in Table 4 and Figure 9.

Figure 9. Permeability (in barrers) for pure PC-PU matrix and for three PC-PU nanocomposites (a) for methane, nitrogen and oxygen; (b) for hydrogen and carbon dioxide. 1 barrer = \(10^{-10}\) cm\(^3\) (STP) cm cm\(^{-2}\) s\(^{-1}\) cm Hg\(^{-1}\).

Permeability was measured by static method [54] and diffusion coefficients and solubility were calculated from the time lag \(\Theta\). It follows from Table 4 and Figure 9 that the permeability of gases is not significantly affected by the addition of nanofillers. Only the nanofiller A7 slightly decreases permeability of all gases. This phenomenon can be explained by the barrier effect of perfectly dispersed small nanofiller particles in PU matrix which partially blocks and prolongs the passage of gas molecules through the matrix. The fact that the gas molecules pass through PU matrix is also confirmed by the separation coefficients of different gas pairs that do not depend on the addition of nanofillers. The values of diffusion coefficient and solubility of gases do not show significant differences. However, it should be noted that the calculation of the diffusion coefficient and solubility values by the time lag
method is affected by significant uncertainty. This occurs especially for hydrogen which has a very short time lag and thus the error can be 50% or even more. On the other hand, the time lag of CO$_2$ is very long and therefore the experimental error in the diffusion coefficient and solubility are small. The size of nanoparticles does not almost affect the gas transport properties; some effect is obvious only for very small particles A7. For given system, GTP are not influenced by particle character (hydrophilic vs. hydrophobic). Particle size between ca. 10 to 40 nm has only negligible effect on all GTP. This fact is important for possible practical, e.g. medicinal applications and it is promising especially for hydrophobic A12 nanofiller (cf. part Tensile properties).

**Conclusion**

The chapter shows that even small amounts of silica nanoparticles (1 wt. %) can considerably influence functional properties of polyurethane nanocomposites.

WAXD revealed that the size and character of nanoparticles does neither substantially influence their internal arrangement in the nanocomposite material nor intrinsic organization of (segmented) polyurethane matrix. TEM confirmed that smaller particles (hydrophilic 7 nm and hydrophobic 12 nm) are dispersed in PU matrix in the form of agglomerates of ca 1 µm size, while hydrophilic 40 nm particles are present in the form of smaller formations (up to 0.5 µm). The surface morphology of the film analyzed by AFM is affected only by the size of particles: the smaller particles, the higher surface roughness (scale $10^1$ to $10^2$ nm). The presence of nanoparticles has only negligible influence on gas transport properties.

Mechanical properties depend both on the size and on the character of nanoadmixtures. All particles interact preferably with hard segments, as detected from dynamic mechanical thermal analysis. From tensile characteristics follows that hydrophobic 12 nm particles are very efficient nanoadditive for the preparation of very elastic and simultaneously high tough nanocomposite polyurethane-based coating/film.

**Acknowledgments**

The authors wish to thank the financial support of Czech Science Foundation (GAČR, project 13-06700S). Experimental work of Mrs. J. Hromádková (TEM), Dr. A. Zhigunov (WAXD) and MSc. J. Hodan (tensile analysis) is acknowledged as well.

**References**


The Influence of the Size, Shape and Character of Nanofillers …


