



Mechanical and thermomechanical properties of polycarbonate-based polyurethane-silica nanocomposites

Rafał Poreba^{1,*}, Milena Špírková¹, Zdeněk Hrdlička²

¹*Institute of Macromolecular Chemistry AS CR, v.v.i., Nanostructured Polymers and Composites Department, Heyrovsky Sq. 2, Prague 162 06, Czech Republic*

²*Department of Polymers, Institute of Chemical Technology, Technická 5, Prague 166 28, Czech Republic*

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Abstract

In this work aliphatic polycarbonate-based polyurethane-silica nanocomposites were synthesized and characterized. The influence of the type and of the concentration of nanofiller differing in average particle size (7 nm for Aerosil 380 and 40 nm for Nanosilica 999) on mechanical and thermomechanical properties was investigated. DMTA measurements showed that Nanosilica 999, irrespective of its concentration, slightly increased the value of the storage shear modulus G' but Aerosil 380 brings about a nearly opposite effect, the shear modulus in the rubber region decreases with increasing filler content. Very high elongations at break ranging from 800% to more than 1000%, as well as high tensile strengths illustrate excellent ultimate tensile properties of the prepared samples. The best mechanical and thermomechanical properties were found for the sample filled with 0.5 wt.% of Nanosilica 999.

Keywords: fumed silica, polycarbonate diol, nanocomposites, polyurethane

I. Introduction

Polyurethane elastomers are block copolymers that consist of hard and soft microdomains. As soft segments, numerous substances can be used e.g. polyether, polyester or polycarbonate macrodiols. The urethane hard segments are typically composed of a diisocyanate and a low molecular weight diol or diamine as a chain extender. The soft segments are responsible for the flexibility of the polymer backbone, while hard units provide physical crosslinks by intermolecular association through hydrogen bonding [1–3]. Phase separation between hard and soft segments and the ability of hard segments to form hydrogen bonds between themselves strongly depend on the hard segment content [4].

Polyurethanes based on polycarbonate diols exhibit excellent mechanical properties like tensile strength, modulus and higher resistance toward hydrolysis in comparison with similar ones based on polyesters [5]. These properties are assigned to a high degree of

phase mixing due to hydrogen bonding between soft segment carbonate groups and hard segment urethane groups [6,7].

Polymer-based nanocomposites are particle-filled polymers where at least one dimension of the dispersed particles (usually ceramics phase) is in the nanometer range [8]. The properties of nanocomposites strongly depend on the organic matrix, nanoparticles content, their size and shape, and also on the way of a nanocomposite preparation [9,10]. Recently we reported in more details the composition-property relationship and also the influence of different clays addition on thermal properties of polyurethanes based on polycarbonate diols with M_w about 1000 [11,12]. In this work, we investigated the influence of silica nanofiller type and concentration on mechanical and thermomechanical properties of polyurethane-silica nanocomposites based on polycarbonate diol with M_w 2000.

II. Experimental

The aliphatic polycarbonate diol with molecular weight around 2000, “T5652” (MD), donated kindly by Asahi Kasei Chemical Corporation was used as

* Corresponding author: tel: +420 296 809 285
fax: +420 296 809 410, e-mail: poreba@imc.cas.cz

the source of elastic chains. Hexamethylene diisocyanate (HDI), butane-1,4-diol (BD) as a chain extender of hard segments and catalyst dibutyltin dilaurate (DBTDL), were supplied by Fluka. Two nanofillers based on fumed silica, “NanoSilica Powder Grade 999” (“N40”, average particle size 40 nm, specific surface area 50 m²/g) from Elkem Silicon Materials, and “AEROSIL® 380” (“A7”, size 7 nm, area 380 m²/g) from Evonik Industries AG, were used.

All samples in the form of sheets and films were prepared using a one-step procedure with constant ratios r and R ($r = [\text{NCO}]/[\text{OH}] = 1.05$ and $R = [\text{OH}]_{\text{MD}}/[\text{OH}]_{\text{BD}} = 1$). The catalyst concentration was 0.005 wt.%. The weight percentage of silica nanofiller was changing from zero for neat polyurethane matrix up to 3.5%. After degassing the mixture containing macrodiol, chain extender and catalyst, the isocyanate component was added; then again the mixture was degassed and poured into Teflon moulds. The samples containing silica nanofiller were prepared by the same procedure. The dispersion of nanofiller was achieved by one day swelling in macrodiol and butanediol mixture and a brief mixing before addition of isocyanate component. The procedure for a film preparation was the same, only the final mixture was spread on polypropylene sheets instead of putting into the Teflon moulds. All samples were kept in nitrogen atmosphere at 90°C for 24 h. The final thickness of PU sheets was 2 ± 0.1 mm and of PU films 0.5 ± 0.05 mm.

Dynamic mechanical thermal analysis was carried out on ARES-LS2 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 from -100 to 150 °C (depends on the sample), at a heating rate of 3 °C/min. Dynamic torsion measurements were performed using rectangular samples, with applied constant tension force of 5 g. The standard specimens' dimensions were 10 mm × 9 mm × 2 mm.

In order to investigate the static mechanical properties of prepared PU films, an Instron model 3365 (Instron Limited, UK) was used. The dimensions of measured samples were: width ~8 mm, total length ~40 mm and gauge length (length of the film between the grips) 20 mm. The thickness was 0.5 ± 0.05 mm, according to particular film. The test was performed with the speed of 10 mm/min. Presented values are averages obtained from at least five specimens.

III. Results and discussion

3.1. Dynamic mechanical thermal analysis (DMTA)

The temperature dependence of storage shear modulus G' of the prepared nanocomposites is shown in Figs. 1-4. The samples show generally similar G' =

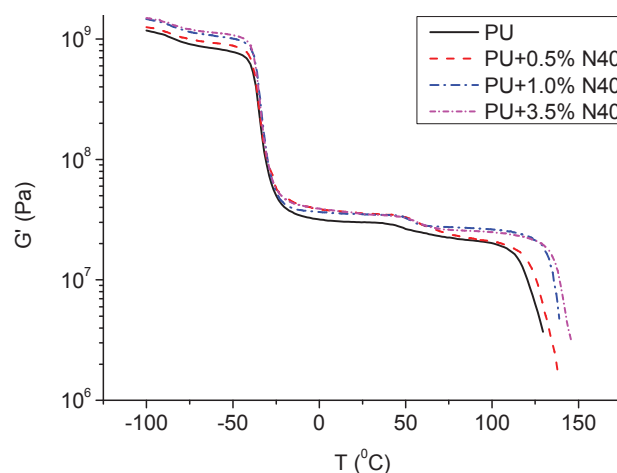


Figure 1. Influence of silica-N40 concentration on storage shear modulus G'

$f(T)$ profiles: in the glassy region, a secondary relaxation near -70 °C can be observed, corresponding to the segmental mobility of carbonate units in glassy polycarbonate diol. Transition, near -30 °C, which is assigned to the glass transition of the polycarbonate diols as soft segments, is observed. Due to physical crosslinks originating from hard segments (which are formed from hexamethylene diisocyanate and chain extender butane-1,4-diol), the samples are in rubbery state beyond the glass transition of polycarbonate chains. In the rubber region, one small transition can be observed near $+50$ °C, which is probably connected with the breaking of relatively weak physical crosslinks between hard segments and the polycarbonate diol soft segments. Finally, the last transition is observed around 140 °C, corresponding to the dissolution of crosslinks between hard segments and hence to sample melting.

At the smallest silica filler concentration, only the physical crosslinking between hard and soft segments seems to be strengthened (the increase of G' in the cor-

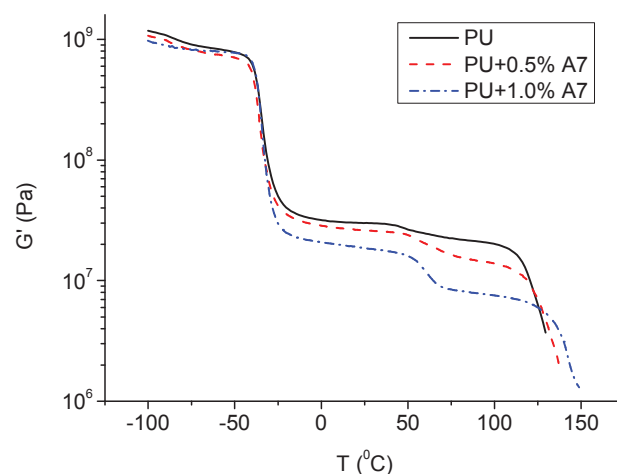


Figure 2. Influence of silica-A7 concentration on storage shear modulus G'

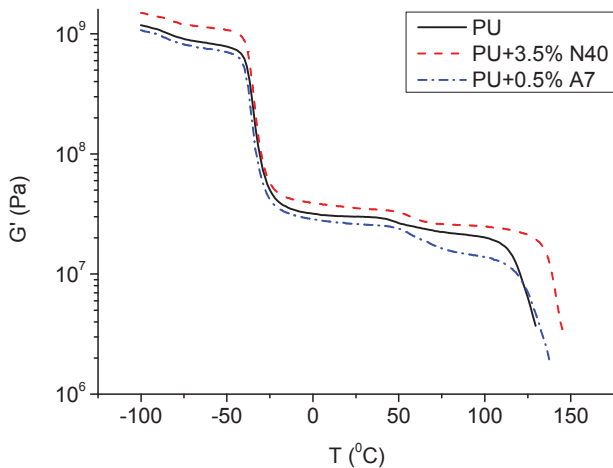


Figure 3. Comparison of samples with approximately the same surface area of nanofillers

responding part of rubber plateau). At higher silica-N40 concentrations, the hard-hard segment interactions are also strengthened and the ultimate melting temperature increases. The nanofiller effect reaches “saturation” at around 1 wt.%; there is a little difference between samples containing 1 and 3.5 wt.% of silica-N40.

The incorporation of silica-A7 brings about a nearly opposite effect, if compared with silica-N40. Generally, the shear modulus in the rubber region rapidly decreases with increasing of silica-A7 concentration. Especially, the hard-hard interactions are weakened by addition of this nanofiller (considerable decrease of G' in the corresponding part of rubber plateau). The negative effect of this filler does not reach “saturation” at a few wt.% (like for silica-N40). The samples containing more than 0.5 wt.% of silica-A7 become very brittle; the specimen with 3.5 wt.% of silica-A7 was too brittle to be measured.

The opposite effects of silica-A7 and silica-N40 in the nanocomposites with polycarbonate based poly-

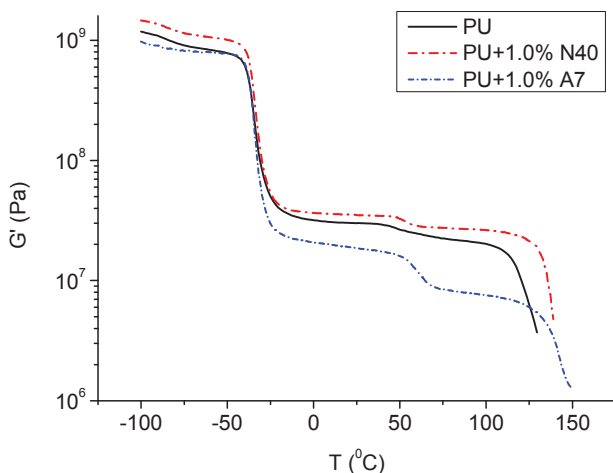


Figure 4. Samples containing the same concentration of nanofillers

urethanes are demonstrated in Figs. 3 and 4. In the first case, samples containing the same surface area of the both nanofillers are compared, and their effects are approximately symmetrically opposite. The addition of silica-A7, however, does not shift the melting temperature significantly in any direction. In case of the same weight loading, the destabilizing effect of silica-A7 is much stronger than the stabilizing effect of silica-N40, due to higher specific surface area of silica-A7.

3.2. Tensile properties

The tensile properties i.e., tensile strength, elongation at break and toughness¹ of examined polyurethanes and their nanocomposites are listed in Table 1. Experimental tensile curves (shown in Figs. 5 and 6) are closest to the average values.

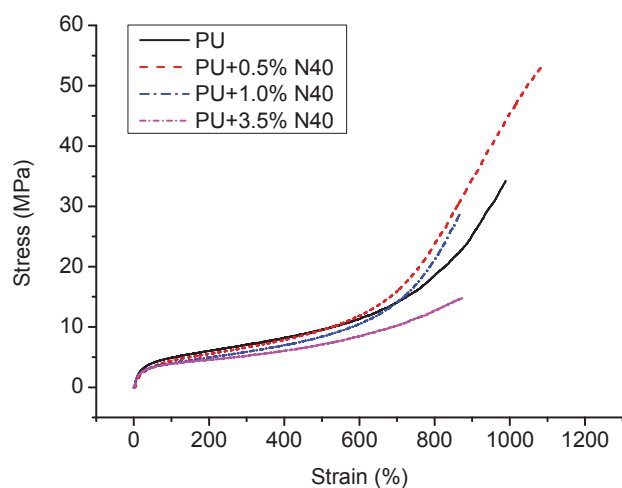
A typical profile of tensile curves begins with small region of true elasticity at which no uncoiling of polymer chains occurs. Elastic deformation at this region is related to hydrogen bonds between hard urethane segments like also between hard urethane and soft polycarbonate segments. Urethane groups contain simultaneously H-donor (NH) and H-acceptor (C=O) while polycarbonates possess only H-acceptor (C=O) units. At higher deformations, breaking of H-bonds of hard and soft segments takes place; samples yield and the polymer chains begin uncoil. In this region, only moderate increase of stress with increasing strain is observed. At high elongations, from around 600%, so called “stress-induced crystallization” takes place and strengthening of the samples occurs, probably due to easier formation of new hydrogen bonds between highly oriented and aligned polymer chains. In this region (beginning from around 900% elongation), the samples finally break.

Among the samples filled with silica-N40, only the one with 0.5 wt.% of nanofiller displays an improvement of tensile properties. Both elongation at break and tensile strength are higher for the nanocomposite than for the neat matrix (see Table 1). With increasing amount of nanofiller, a decrease of all tensile properties is observed. The samples filled with silica-A7 were very brittle, only the one with the lowest nanofiller content (0.5 wt.%) could be well characterised. Incorporation of silica-A7 brings about a different, partly opposite effect than silica-N40, if the samples with 0.5 wt.% of nanofillers are compared. The sample with 0.5 wt.% of silica-A7 displays markedly lower tensile strength than the neat matrix (opposite effect to silica-N40) but increased elongation at break (similar to silica-N40). However, with an increase of silica-A7 content, the tensile properties rapidly deteriorate (impossibility of reasonable tensile characterisation of the brittle samples).

¹ Toughness is defined as the amount of energy per unit volume that can be adsorbed by a material before rupturing.

Table 1. Tensile properties of unfilled and silica filled PU elastomers in form of films

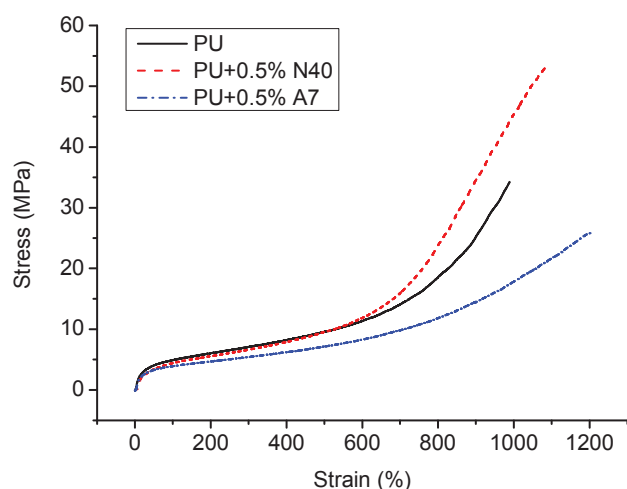
Sample	PU	PU + 0.5% N40	PU + 1% N40	PU + 3.5% N40	PU + 0.5% A7
Concentration [wt.%]	-	0.5	1	3.5	0.5
Tensile strength [MPa]	36.5	50.9	30.7	13.3	19.2
Strain at break [%]	994	1094	828	933	1083
Toughness [mJ/mm ³]	112	126	85	60	96

**Figure 5. Influence of silica-N40 concentration on tensile properties**

IV. Conclusions

In this work, synthesis of aliphatic polycarbonate-based polyurethane-silica nanocomposites with good mechanical and thermomechanical properties was achieved.

In all cases of samples filled with silica-N40 a higher storage shear modulus G' and melting temperatures were observed whereas the samples loaded with silica-A7 showed reduced values of modulus G' . The addition of silica-A7, however, does not shift significantly the melting temperature in any direction. The samples

**Figure 6. Influence of filler type on tensile properties**

filled with more than 1 wt.% of silica-A7 were too brittle to be measured.

Tensile properties can be improved by incorporation of small amounts of silica-N40, i.e., 0.5 wt.% into the neat matrix. Incorporation of the same weight load of silica-A7 brings about a drop of tensile strength simultaneously with the increase of elongation at break, in comparison with neat matrix. Generally, (the exception mentioned above) increasing concentration of nanofiller (regardless of type of silica), both elongation at break and tensile strength decrease, hence lead to lower toughness values.

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