

Influence of Nanosilica on the Morphology, Thermal and Mechanical Properties of Polyurethane Elastomer

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ABSTRACT: In this article, the influence of fumed silica nanofiller on the structure and properties of segmented polyurethane elastomer (PUR) was investigated. In order to investigate the interactions at the filler–matrix interface, nonmodified and commercially modified fillers (with methacrylsilane and octylsilane) were used. The PUR composites with 1.0, 2.0, 4.0, 6.0, and 9.0 vol % of all fillers were prepared by solution casting method. Surface free energy of the fillers and polymer matrix was determined using contact angle measurements with different testing liquids. Change in morphology was analyzed using optical polarization microscopy and distribution of the filler in polymer matrix using scanning electron microscopy. The influences of silica fillers on mechanical and thermal properties of PUR were investigated. Results showed that sur-

face treatment of silica filler with methacrylsilane and octylsilane reduces the agglomeration of particles that improves dispersion at microlevel. Addition of all fillers disrupts spherulite morphology and decreases crystallinity of the PUR matrix. Nonmodified silica nanofiller has the least pronounced influence on spherulite morphology and the lowest influence on polyurethane crystallinity and thus the best mechanical properties. Surface modification of silica with octylsilane has less influence on polyurethane crystallinity and on decreasing of mechanical properties than modification with methacrylsilane. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E181–E190, 2012

Key words: composites PUR/silica; silane-modified fumed silica; morphology; thermal properties; mechanical properties

INTRODUCTION

Polyurethane elastomers play an important role in various fields of applications. Because of superior properties related to their high hardness for a given modulus, high abrasion resistance, excellent mechanical properties, and biocompatibility, polyurethanes found application in many fields of adhesives, optoelectronic, biotechnology, and many others.^{1,2} Polyurethane elastomers are block copolymers, consisting of rigid and flexible segments. Because of the difference in polarity, that is, thermodynamical incompatibility, these segments separate into soft and hard phases. Widespread application of the polyurethane elastomers is a reason for extensive research carried out in the fields of novel type synthesis and structure–properties relationship.^{3–5}

The addition of the inorganic filler to polymer material has significant influence on the properties of material. When compared with microsize fillers, nanosize fillers have higher specific surface area and considering added amount can achieve great contact with polymer matrix. Thus, previous research has

shown that by decreasing the particle size of silica fillers more significant impact on properties of polyurethane can be achieved.^{6–8} In addition, silica filler has more pronounced effects on the properties of elastomeric than on glassy polyurethane.⁹

Fumed silica is a synthetic, amorphous material that has spherical particles which are, depending on the conditions of synthesis, in the range 7–30 nm.¹⁰ Depending on the size of primary particles, specific surface area is in the range 100–400 m² g⁻¹. Primary fumed silica particles form chain-like, branched aggregates. Because of the silanol groups on the surface, silica filler is hydrophilic.¹⁰ Surface of silica filler can be modified with different agents and thus modified filler enable tailoring of interface properties and as consequence properties of material as a whole. Different types of silanes are commonly used for surface modification of silica. The replacement of silanol groups that are hydrophilic with dimethylsilyl, trimethylsilyl, or octyl groups changes hydrophilic nature of filler surface into hydrophobic.¹⁰ Silica fillers modified with the silanes are commercially available.

Fumed nanosilica has significant applications as filler in many important products (paints, coatings, pigments, adhesives, etc.) based on polyurethane, epoxy, silicone, polychloroprene, acrylic and so on.¹⁰ In products, the use of fumed silica will confer thixotropy, sag

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resistance, particle suspension, emulsifiability, reinforcement, gloss reduction, flow enhancement of powders, anticaking, antiblocking and so on. Because of its effect on these important properties, fumed silica is widely used in many industries.¹⁰ For example, earlier studies have shown that the addition of nonmodified fumed silica filler to the polyurethane adhesive solutions modifies its rheological properties and significantly increases the peel strength of chlorinated rubber adhesive joints.^{11–13}

Interface between the polymer matrix and the filler is extremely important for the final properties of polymer composites. Our previous studies have shown that engineering the surfaces of fillers can tailor the interfacial properties of polymer/filler and thus optimize the material properties as a whole.^{14–16}

In recent years, polyurethane/fumed silica nanocomposites have been studied extensively.^{17–23} The results showed that the addition of nanosilica improves thermal, rheological, mechanical, and adhesion properties of polyurethanes. This enhancement is attributed to the formation of hydrogen bonds between the silanol groups on the nanosilica surface and the ester carbonyl groups in soft segments.^{17–19} Thus, addition of nanosilica to polyurethane enhances the incompatibility between hard and soft segments favoring the phase separation.^{21,22}

The aim of this study was to explore how addition and surface modification of silica filler affect on the structure and properties of polyurethane elastomers. With the aim to investigate the influence of the interface of two-phase polyurethane elastomer, nonmodified silica and silica modified with methacrylsilane and octylsilane were used as fillers. The effects of these fillers on the morphology and mechanical and thermal properties were investigated.

EXPERIMENTAL

Materials

For sample preparation, predominantly linear hydroxyl polyester polyurethane elastomer matrix (Desmocoll 620, produced by Bayer, Germany) in form of granules was used. Three different fumed nanosilicas (Table I) manufactured by Degussa, Germany, were used as fillers for nanocomposite preparation. According to manufacturer specifications, nominal primary particle size of Aerosil 200 is 12 nm. The modified fillers were obtained by modifying the surface of filler Aerosil 200 with methacrylsilane (Aerosil R711) and octylsilane (Aerosil R805).

Nanocomposite preparation

The PUR nanocomposites samples were prepared by solvent casting method. A certain amount of PUR

TABLE I
Properties of Fumed Silica

Filler	Surface modification	Specific surface area, S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Tamped density (g L^{-1})
Aerosil 200	–	200	50
Aerosil R 711	Methacrylsilane	150	60
Aerosil R 805	Octylsilane	150	60

granules and the filler is mixed with acetone in a ratio (PUR : acetone = 1 : 5). The mixture was swollen the next 24 h and then homogenized 3 h on a magnetic stirrer at 250 rpm. Homogenized mixture is left to dry at room temperature in a covered Petri dish to prevent rapid evaporation of acetone, which would cause porosity of the film. The sample was left to dry until the complete evaporation of acetone. This procedure has been used to prepare samples without fillers and composites with 1, 2, 4, 6, and 9 vol % of all three fillers.

Experimental techniques

Optical polarization microscopy

Morphological structure was examined using polarization microscope equipped with a Leica camera Sony on microtomed samples. Thin samples were placed on glass slide, fixed with cedar oil, and covered with a coverslip.

Scanning electron microscopy observations

Surface of PUR composites with 9 vol % nonmodified and octylsilane- and methacrylsilane-modified fillers were analyzed using scanning electron microscope FEI Quanta 200. Dispersion of fillers in the composite sample was analyzed by the filler's silicon mapping using the EDX detector "Eagle system."

Tensile testing

Tensile testing of PUR nanocomposites was carried out on a Universal testing machine Zwick 1445 at $T = 25^\circ\text{C}$ and $\text{Rh} = 50\%$. Prepared samples were cut into strips with width of 6 mm, length of 100 mm, and a thickness of 0.8 mm. Part of the specimen subjected to stress was in the length of 50 mm. Tensile testing was carried out at cross-head rate of 100 mm min^{-1} . From obtained curves, values of Young modulus (E), stress at break (σ_b), elongation at break (ε_b), and work to break (W_b , area under tensile curve) were determined.

Differential scanning calorimetry

Samples of pure PUR and prepared composites were investigated by differential scanning calorimetry

TABLE II
Surface Free Energy (γ) and Its Dispersive (γ^d) and Polar (γ^p) Components of Test Liquids Used for Contact Angle Measurement²¹

Test liquid	γ (mJ m ⁻²)	γ^d (mJ m ⁻²)	γ^p (mJ m ⁻²)
Water	72.8	21.8	51.0
Formamide	58.0	39.0	19.0
Diiodomethane	50.8	50.8	0

(DSC) technique on the instrument DSC 823 Mettler Toledo. Measurements were carried out in two heating runs in the temperature range -90 to 100°C under nitrogen atmosphere (50 mL min^{-1}) in aluminum pans with 9–11 mg of sample.

Determination of surface free energy of composite constituents

The dispersive and polar component of surface free energy of PUR matrix and fillers were determined by contact angle goniometer instrument OCA 20, DataPhysics Instruments at temperature 23°C . The instrument is equipped with automatic drop dosing system and camera for recording drop at the sample. Determination of the free energy of the filler surface was carried out at disk-shaped samples of pressed fillers, and the free energy of PUR matrix was measured on a film of pure polyurethane. To determine the dispersive and polar component of the surface free energy of PUR matrix and fillers the test liquids water, formamide and diiodomethane were used. Dispersive and polar components of surface free energies of test liquids²⁴ are given in Table II. Contact angle between liquid drop and tested sample was determined immediately after application of liquid drop. From the measured values of contact angles and the known values of the surface free energy used for the test liquids (Table II), according to Wu model^{25,26} [eq. (1)] dispersive and polar components of the surface free energy were calculated using software OCA 20.

$$\gamma_l(1 + \cos \theta) = \frac{4\gamma_l^d\gamma_s^d}{\gamma_l^d + \gamma_s^d} + \frac{4\gamma_l^p\gamma_s^p}{\gamma_l^p + \gamma_s^p} \quad (1)$$

RESULTS AND DISCUSSION

Surface free energy of composite constituents

In this article, the surface free energy of the fillers was determined in order to understand the potential effects of filler surface modification on morphology, structure, and properties of polyurethane/silica nanocomposites. Contact angle measurement is a common method for evaluating the surface energy of solids.²⁴

Contact angles with test liquids (water, formamide, and diiodomethane) and surface free energies of the unmodified (A200) and modified (A711, A805) silica fillers are given in Table III. The dispersive γ^d and polar γ^p components of the surface free energy were calculated by using eq. (1). Dispersive and polar components of the unmodified filler (A200) are high due to the presence of the $-\text{OH}$ groups at the surface of the filler. Because of the treatment of silica surface with methacrylsilane filler A711 has significantly smaller polar component of surface free energy in comparison to hydrophylic silica filler A200. However, A711 exhibits some degree of polarity due to polar carbonyl $-\text{C}=\text{O}$ group in the methacrylsilane, that is, this filler has electron acceptor properties. Filler A805, modified with octylsilane, has very low dispersive component and significantly lower polar component in comparison with unmodified hydrophilic A200 filler (Table III). Values of surface free energies of the filler A805 indicate hydrophobic character of the surface of this filler and as a consequence this filler has high value of contact angle with water (Table III). One can assume on the basis of obtained values of surface free energy that the filler modified with octylsilane will establish dispersive interaction with the nonpolar soft phase of polyurethane matrix.

Obtained results of contact angle indicate significant changes of the surface free energy due to modification of the surface with different silanes. Therefore, one can expect that the surface modification of silica fillers with silanes will have an impact on the structure and properties of polyurethane nanocomposites.

The interface between polymer matrix and filler in composite materials has an important influence on the properties of composite. Based on the adsorption theory of adhesion, at the matrix/filler interface dispersive and polar interaction were established. Our previous studies^{14–16} have been shown that properties of composite systems significantly depend on adhesion parameters related to the interface between the polymer matrix and filler. Effective adhesion at the interface imply certain adhesion parameters as optimal, that is, interfacial free energy as minimal (tends to zero), high work of adhesion and positive

TABLE III
Contact Angles with Test Liquids and Surface Free Energies of the Silica Fillers and PU Matrix

Sample	Contact angle ($^\circ$)			Surface free energy (mJ m ⁻²)		
	Water	Form	Dim	γ^d	γ^p	γ
Aerosil 200	0.0	13.6	15.5	40.7	35.5	76.2
Aerosil 711	86.7	49.1	27.5	44.5	4.6	49.1
Aerosil 805	147.8	148.1	48.2	15.0	0.5	15.5
PUR 620	92.9	74.7	53.9	31.4	3.1	34.5

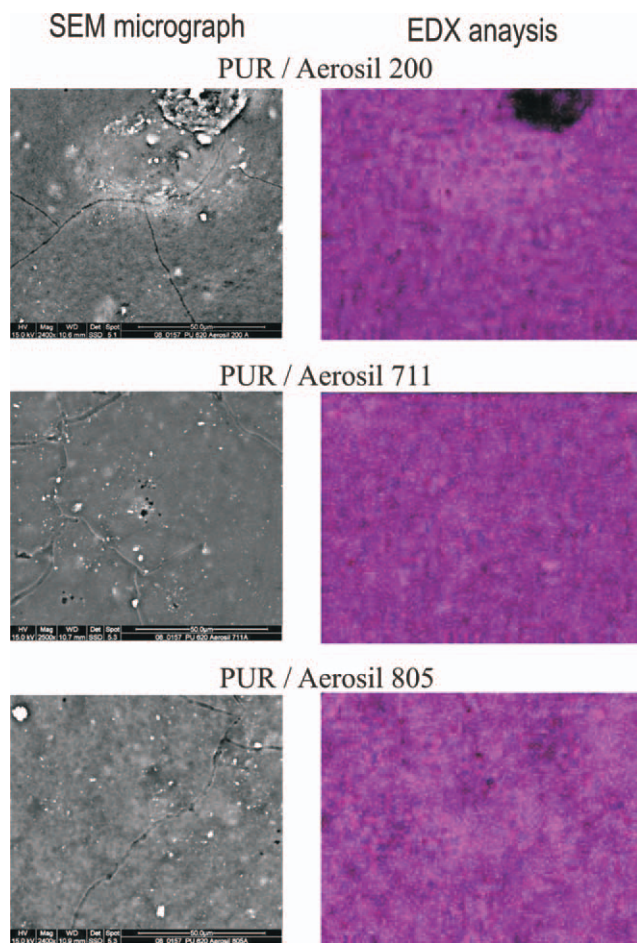


Figure 1 SEM micrographs and EDX pictures of the PUR/silica nanocomposites with 9 vol % of filler and Si atoms mapping. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coefficient of wetting. However, the approach that uses the optimal parameters of adhesion for the systems in which the polymer matrix has a nonpolar soft phase and a rigid polar phase, as in PUR, has certain drawbacks. According to this approach, it is not possible to distinguish the difference in polarity between hard and soft phases of the PUR matrix. Therefore, this approach is not useful for determining the characteristics of the interphase in the investigated PUR/silica nanocomposites.

Dispersion of SiO₂ nanofiller in the PUR matrix

Dispersion of the nanofiller in PUR matrix is one of the most important factors that crucially influence on the properties of the nanocomposites. The dispersion of silica fillers in polyurethane matrix was analyzed using scanning electron microscopy (SEM) equipped with EDX detector. Micrographs and EDX pictures of the PUR nanocomposites with 9 vol % nonmodified filler (A200) and modified fillers (A711 and A805) are presented at Figure 1.

Preparation method of nanocomposites significantly affects the dispersion of fillers in the polymer matrix. For example, much more homogeneous distribution of silica filler in the PUR matrix can be achieved by method of preparation *in situ* than with preparation by blending method.^{7,27} By solvent casting method used for nanocomposite preparation in this work, all fillers are homogeneously distributed in PUR matrix in a form of aggregates. Additionally, at all nanocomposite micrographs, some structures, few micrometers large, are visible. However, at those places in the EDX pictures, there are no higher intensity of Si signal, thus indicating that are not large agglomerates of filler. SEM/EDX micrograph in Figure 1 indicates that surface treatment of silica filler reduces the agglomeration of particles that improves dispersion at microlevel.

Morphology of PUR/silica nanocomposites

The effect of silicas with different surface modification on the phase morphology of PUR was investigated by polarization microscopy. Depending on the monomers used for synthesis, the proportion of soft and hard segments and method of sample preparation the morphology of segmented polyurethane can be in the form of spherulites, grains, or elongated morphological forms that look like granular aggregates.²⁸ Polarizing micrographs of pure PUR (Fig. 2) indicate well-developed polygonal spherulite morphology. Maximal anisotropic diameter of the spherulites measured from the micrographs was 40 μm .

The incorporation of nanoparticles in a semicrystalline polymer matrix usually affects its morphology.^{29,30} Change of morphology with incorporation of silica fillers is illustratively shown at polarizing micrographs of PUR/silica nanocomposites in Figures 3 and 4. The micrographs of composites in

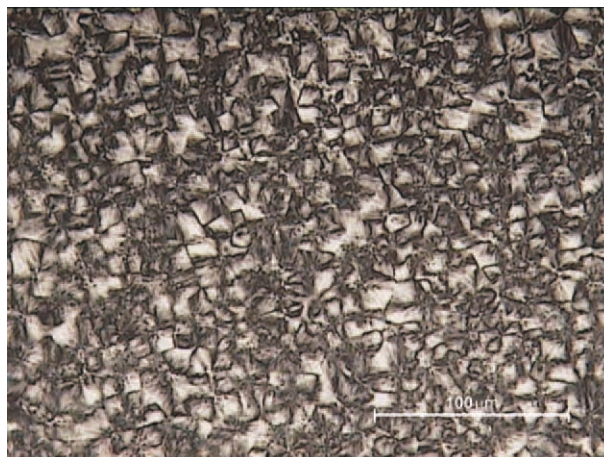


Figure 2 Polarizing micrograph of PUR matrix. Scale bar represents 100 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

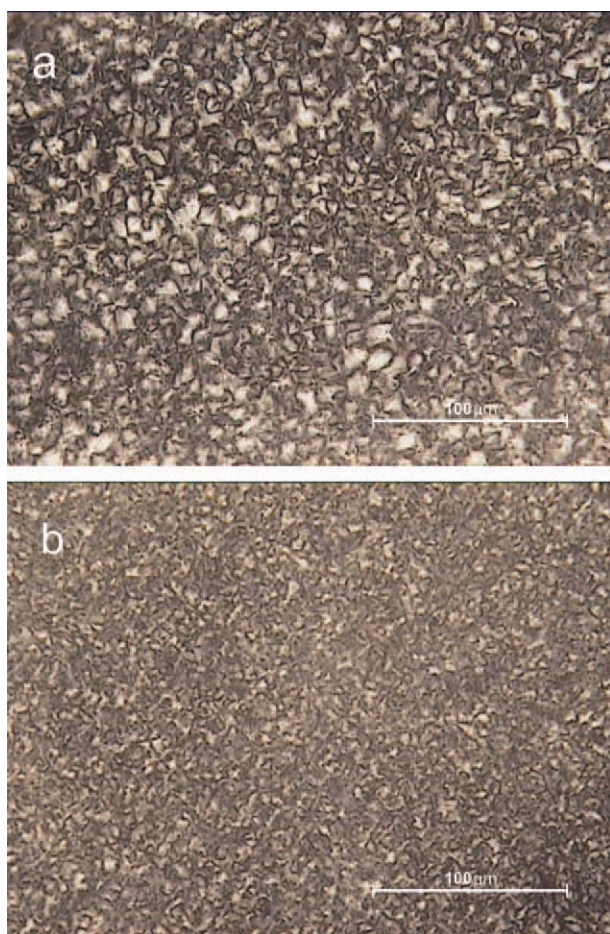


Figure 3 Polarizing micrograph of PUR/Aerosil 200 nanocomposites with different volume fraction of filler (a) 4% and (b) 9%. Scale bars represent 100 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 revealed the decrease of spherulite size and their disturbing with addition of hydrophilic A200 nanofiller. Spherulites are still visible up to 4 vol % of added silica A200 filler [Fig. 3(a)], but further addition of filler above 4 vol % causes the transition of spherulites into irregular elongated forms up to grain morphology [Fig. 3(b)]. A similar effect of substantial decrease in the spherulites size up to fine spherulitic or even grain morphology was also observed in the same PUR matrix with incorporation of nano- CaCO_3 .³¹ This change in morphology can be assigned to the nucleating ability of filler particles. Filler particles can act as heterogeneous nuclei during crystallization of polymer matrix. Thus, by increasing the fraction of filler in composite increases the heterogeneous nuclei density and decreases of spherulite size. Somewhat different approach was proposed by Manias et al.³⁰ According this approach, changes in spherulite morphology due to nanofiller addition originate from the discontinuity of space caused by the inorganic fillers, which forces

spherulites to have sizes comparable with the filler-filler separation, independent of the bulk polymer spherulite size. This effect is also independent of whether crystallization in the nanocomposite is nucleated homogeneously or heterogeneously, and of whether the fillers hinder crystallization, promote new crystal structures, or simply act as heterogeneous nucleating agents.³⁰

Polarizing micrographs of nanocomposites with silica filler modified by methacrylsilane (A711) and octylsilane (A805; Fig. 4) indicate that surface modification of silica affect the morphology of PUR matrix stronger than unmodified hydrophilic A200 filler (Fig. 3). Furthermore, polarization micrographs show that different types of silane used for silica surface treatment has different impact on morphology. Silica nanoparticles modified with octylsilane [Fig. 4(c,d)] has a more prominent effect on disrupting the spherulite morphology than nanosilica modified with methacrylsilane [Fig. 4(a,b)]. The observed effect of surface modification of silica on the spherulite morphology can be assigned to changes of surface free energy of fillers and thus its compatibility with the polyurethane matrix. DSC analysis showed that in the investigated PUR matrix soft segment crystallizes. Therefore, the changes of surface energy of fillers were analyzed from the standpoint of compatibility with the soft segment of polyurethane matrices. With increasing hydrophobicity of the filler, its compatibility with crystalline nonpolar soft segment of PUR matrix increases and as consequence nucleating ability of filler increases as well. Thus, the hydrophobic filler A805 has the strongest nucleating ability that results in the smallest spherulites [Fig. 4(c,d)].

Thermal properties of PUR/silica nanocomposites

The influence of amount and character of silica filler surface on crystallinity of PUR matrix was investigated using DSC. Thermal properties of the PUR matrix and PUR/ SiO_2 composites were investigated in two heating cycles. Thermogram of PUR matrix presented in Figure 5 indicates T_g of soft segments at -42.9°C and melting of soft segments T_m (I) at 45.9°C . During cooling (rate $10^\circ\text{C min}^{-1}$) after first heating cycle, PUR matrix does not crystallize. In second heating cycle after T_g (II) at the temperature -45.8°C , peak of cold crystallization of soft segments appears at temperature T_{cc} (II) 1.9°C , and then endothermal peak of soft segments melting T_m (II) at the temperature 36.4°C .

Thermal properties in the first heating cycle are related to the structure resulted from slow crystallization process during evaporation of acetone, while in second heating properties are connected with nonisothermal crystallization process. The values of

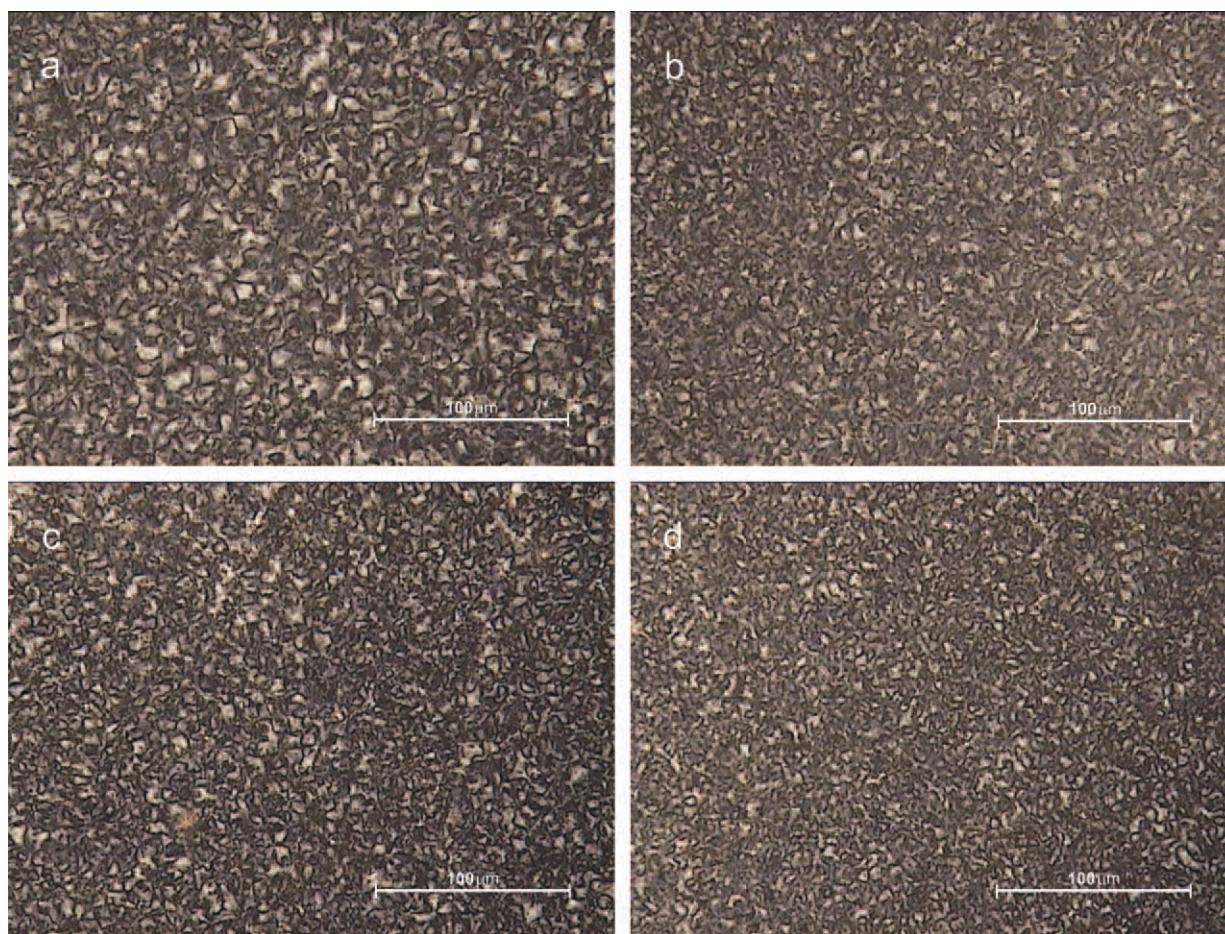


Figure 4 Polarizing micrographs of PUR nanocomposites with (a) 1 vol % of Aerosil 711, (b) 4 vol % of Aerosil 711, (c) 1% of Aerosil 805, and (d) 4% of Aerosil 805. Scale bars represent 100 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

melting temperature T_m (I), T_m (II), and T_g (II) of all investigated PUR/silica nanocomposites vary in range $\pm 2^\circ\text{C}$ in comparison with neat PUR. Obviously, any type and amount of silica filler affects melting temperature slightly, that is, silica filler does not affect perfection the crystallites.

Values of melting enthalpy of soft segments in the first ΔH_m (I) and second ΔH_m (II) heating cycles that correspond to the amount of crystalline phase are presented in the Table IV and Figures 6 and 7. Theoretical values of crystallinity taking into account amount of filler in nanocomposites were calculated according to the additivity rule and are presented at Figures 6 and 7. It may be observed that the addition of all fillers decrease crystallinity of PUR in both heating cycles (Figs. 6 and 7). Results (according Fig. 6) indicate that decreasing of the crystallinity is less pronounced in PUR composites with polar filler A200. These results are consistent with better phase separation due to the interaction between hydroxyl $-\text{OH}$ groups at surface of this filler and the ester carbonyl groups in soft segments and/or polar groups in hard segments. Similar behavior of composites with hydrophobic A805 may

be explained with compatibility of octyl chains and soft segments that induce phase separation as well as pronounced crystallization of soft segments. After first heating cycle follows nonisothermal crystallization that is rather influenced by surface treatment of silica A711 and A805 nanoparticles (Fig. 7) than by phase separation (affecting by A200 and A805) in crystallization processes from solution (Fig. 6).

Effect of silica surface modification on the melting enthalpy in the first heating cycle (Fig. 6) is significantly different from the effects in the second heating cycle (Fig. 7). It is possible that these differences in the degree of crystallinity result from differences in the kinetic of nonisothermal crystallization of polyurethane nanocomposites with nonmodified and silane modified silica fillers. Some indications that modification of silica filler influence on crystallization kinetics of PUR matrix are changes in temperature of cold crystallization (Table IV). Addition of fillers tends to increase cold crystallization temperature T_{cc} (II) compared with the pure PUR matrix thus indicating that silica filler slows down the cold crystallization process of PUR matrix. This effect is

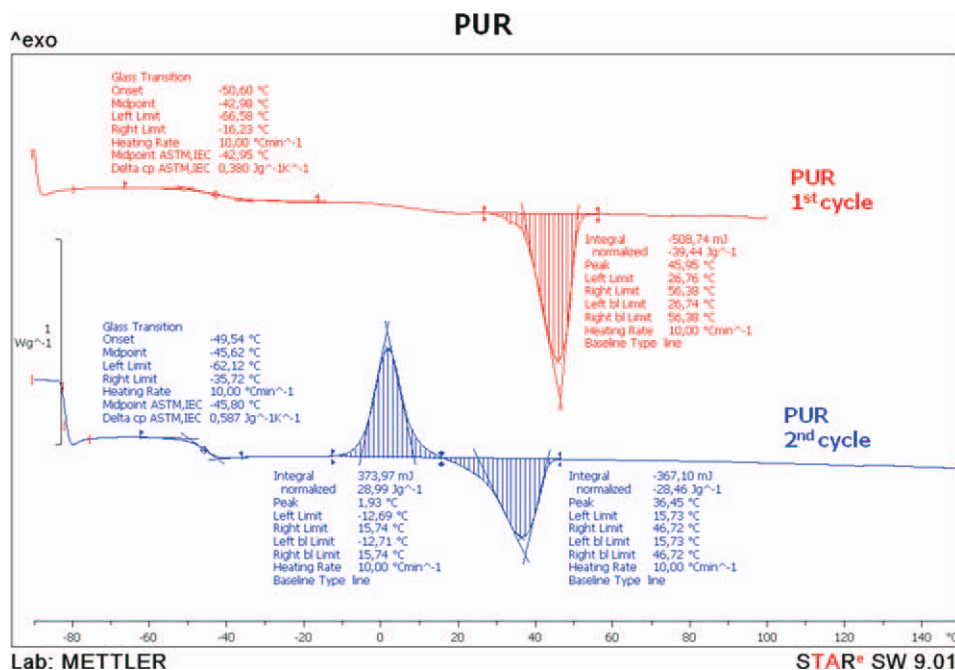


Figure 5 DSC thermogram of PUR matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

more prominent for systems with nonmodified filler (A200), then for systems with the methacrylsilane-modified filler (A711) and at least for systems with filler modified with octylsilane (A805).

Mechanical properties of PUR/silica nanocomposites

In composite materials adhesion at the interface between polymer matrix and filler is an important

factor that influence on the mechanical properties. In this article, influence of modification of silica surface on the tensile properties was investigated. Results indicate that amount and surface modification of silica influence on the mechanical properties of PUR nanocomposites (Figs. 8–11).

At small deformations, adhesion at the interface can contribute to the increasing of Young modulus and yield strength due to the fact that interactions decrease flexibility of polymer chains in the vicinity of the filler surface thus creating interphase in which polymer characteristics are different than in bulk polymer. The addition of all fillers, nonmodified filler (A200) and modified fillers (A711 and A805), increases σ_y and E values in comparison with PUR

TABLE IV
Melting Enthalpy of Soft Segments in the First ΔH_m (I) and Second ΔH_m (II) Heating Cycle and Cold Crystallization Temperature T_{cc} (II) for PUR Nanocomposites

Sample	w (%)	ΔH_m (I) (J g ⁻¹)	ΔH_m (II) (J g ⁻¹)	T_{cc} (II) (°C)
PUR 620	0	-39.4	28.1	1.9
PUR/A200 1%	1.7	-37.3	27.1	3.9
PUR/A200 2%	3.4	-37.4	24.8	7.1
PUR/A200 4%	6.7	-35.7	24.7	4.1
PUR/A200 6%	10.1	-32.0	22.9	5.1
PUR/A200 9%	14.7	-29.9	19.9	6.4
PUR/A711 1%	1.7	-38.2	26.3	6.9
PUR/A711 2%	3.5	-34.8	26.7	2.2
PUR/A711 4%	6.7	-31.8	25.4	2.2
PUR/A711 6%	10.1	-29.3	24.1	3.3
PUR/A711 9%	14.7	-26.8	20.6	5.3
PUR/A805 1%	1.7	-34.9	26.6	2.4
PUR/A805 2%	3.4	-36.1	26.7	2.2
PUR/A805 4%	6.7	-35.2	25.4	0.2
PUR/A805 6%	10.1	-32.3	23.5	4.1
PUR/A805 9%	14.7	-30.2	21.3	5.1

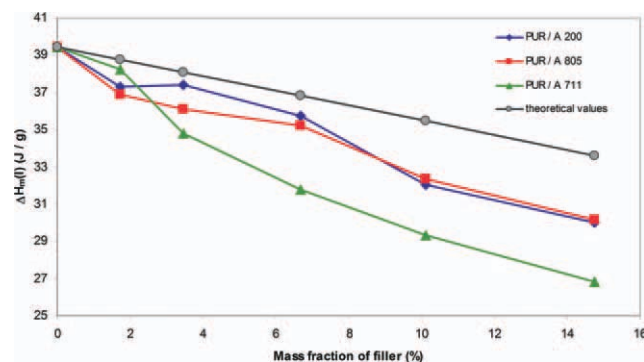


Figure 6 Melting enthalpy of soft segments in first heating DSC scan, ΔH_m (I), of PUR nanocomposites with non-modified and silane modified silicas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

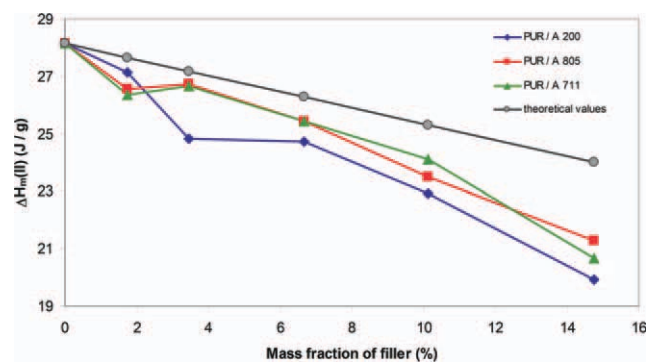


Figure 7 Melting enthalpy of soft segments in the second heating DSC scan, ΔH_m (II), of PUR nanocomposites with nonmodified and silane modified silicas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

matrix. Influence of silica surface modifications as well as amount of silica filler on Young modulus is presented at Figure 8. Results show the highest σ_y and E values in nanocomposites with nonmodified filler (A200). These results can be assigned to the strong interactions at the interface between $-\text{OH}$ groups at silica surface and carbonyl ester group of the PUR matrix. Additionally, as was observed by DSC measurements, due to these interactions the nonmodified silica filler has the least impact on the degree of crystallinity compared with silane modified fillers. Higher values of E obtained for PUR/A805 than for PUR/A711 can be the consequence of the higher degree of crystallinity.

Influence of surface modification and volume fraction of silica on the strength at break, elongation at break, and work to break are presented at Figures 9–11. Investigated nanocomposites with lower volume fractions of filler pulled out from the instrument clamps at high elongation, and it was not possible to obtain breaking values, thus indicating that lower amounts of filler increase strength compared with PUR matrix. In comparison with PUR matrix further addition of all

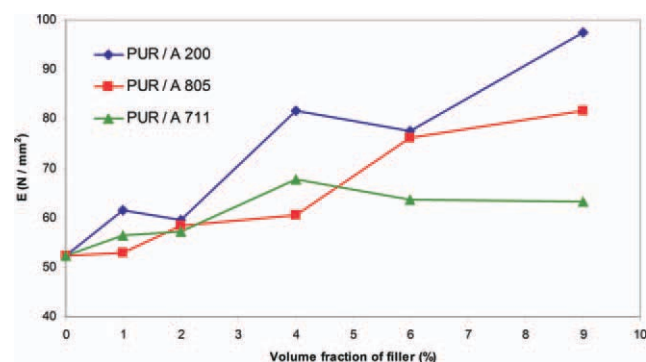


Figure 8 Influence of silica addition and surface modification on Young modulus (E) of PUR/silica nanocomposite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

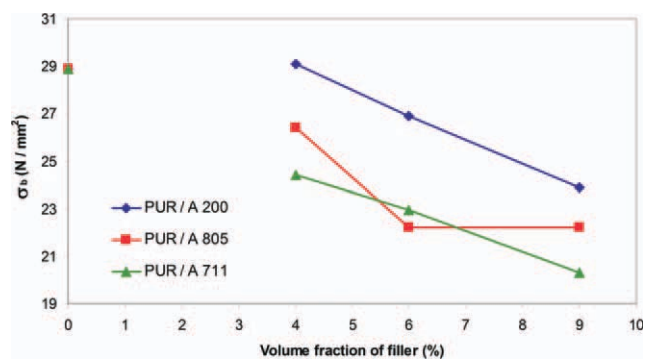


Figure 9 Influence of silica addition and surface modification on strength at break (σ_b) of PUR/silica nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fillers decrease tensile strength (Fig. 9) and elongation (Fig. 10). According to equation proposed by Brostow et al.,^{32,33} decrease of elongation at break implies increasing of composite brittleness and additionally change of tribological properties and impact strength.

In comparison with the nanocomposites with modified fillers, PUR/Aerosil200 nanocomposites have the highest strength at break and work to break values (Fig. 11). These results can be explained by strong interactions between $-\text{OH}$ groups of silica filler and carbonyl ester group of the PUR matrix at the interface. Namely, foreign particles as filler can act as stress concentration points and initiate crack formation that leads to failure and final fracture of material. In systems with strong interactions at the interface, this phenomenon is less prominent. Additionally, nonmodified silica filler affects the crystallization and phase separation in PUR matrix. Stretching up to the high deformations of PUR systems leads to the crystallization.¹⁸ Thus, in systems with a better phase separation, a higher degree of crystallization and higher strength caused by stretching can be expected. The obtained results also show that

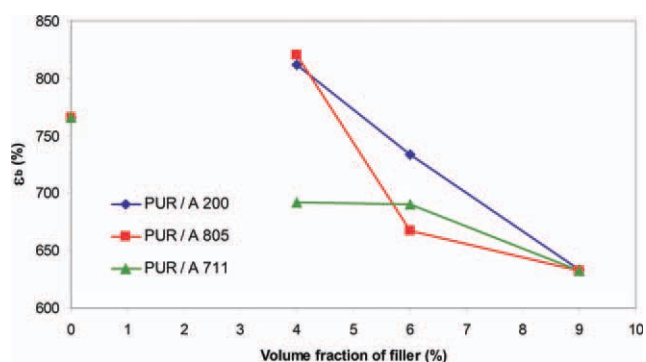


Figure 10 Influence of silica addition and surface modification on elongation at break (ϵ_b) of PUR/silica nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

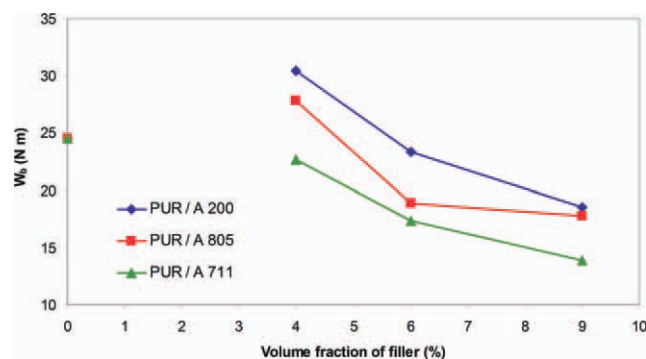


Figure 11 Influence of silica addition and surface modification on work to break (W_b) of PUR/silica nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanocomposites with octylsilane modified silica filler (A805) have a higher work to break values compared with systems with methacrylsilane modified filler (A711) probably due to the higher degree of crystallinity.

CONCLUSIONS

The effect of fumed silica addition and its surface modification with octylsilane and methacrylsilane on the morphology, thermal properties, and mechanical properties of elastomeric polyurethane were investigated. Surface characterization of the fillers indicates significant changes of the surface free energy due to modification of the surface with different silanes. Dispersive and polar components of the nonmodified silica filler (A200) are high due to the presence of the $-OH$ groups at the surface of the filler. Modification of the silica surface with methacrylsilane significantly decreases polar component of surface free energy compared with nonmodified silica filler. However, modification of silica filler with methacrylsilane still offers more polar surface than the modification with octylsilane, which makes this filler hydrophobic and thus more compatible with the nonpolar soft phase of the polyurethane matrix.

Results showed that surface treatment of silica filler with methacrylsilane and octylsilane reduces the agglomeration of particles what improves dispersion at microlevel. The increase in the amount of all silica filler causes reducing of spherulites size and the degree of crystallinity of the polyurethane soft segment. Decreasing of the soft segment crystallinity and reducing the size of spherulites is less pronounced in nanocomposites with nonmodified hydrophilic silica filler. These results can be explained with earlier studies which showed better phase separation in this nanocomposite caused by specific interaction at the PUR/silica interface between the silanol groups on the nanosilica surface

and the ester carbonyl groups in soft segments. Strong interaction at the interface and a higher degree of crystallinity are the reasons for better mechanical properties of nanocomposites with unmodified filler compared nanocomposites with silane modified fillers.

Nanocomposites with octylsilane modified silica in comparison with the nanocomposites with methacrylsilane modified silica have a higher degree of crystallinity of soft segment and better mechanical properties. The obtained results are attributed to the hydrophobic character of octylsilane modified silica and therefore a better compatibility with nonpolar phase of a soft polyurethane matrix.

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