Hybrid Silica Generated *In Situ* in Polyurethane-Based Composites

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ABSTRACT: A series of composites of commercial polyurethane (PU) and hybrid silica have been prepared by the sol-gel process through the *in situ* synthesis of hybrid silica in a solution of dichloromethane. Mechanical properties, small angle x-ray scattering (SAXS) and differential scanning calorimetry measurements were performed to evaluate the effects that hybrid silica has on the properties of the resulting PU composites. A series of 13 different organosilane differing in polarity and alkyl chain length has been employed. Compared with pristine PU, composites bearing hybrid silicas were more likely to exhibit reductions in the yield stress and increase in the elongation at break. Samples also showed a negligible variation in the glass transition temperature and a reduction in the ΔC_p. The enthalpy of the crystallization process showed a trend towards reduction. Based on the SAXS measurements, the composites showed a small reduction in the interdomain spacing, an increase in the degree of phase separation and a tendency towards reduction in the size of the interphase thickness between domains. These results can be better explained as being caused by the volume of the organic group from the organosilane rather than by the chemical interaction of the organic group with the PU organic moieties. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41157.

INTRODUCTION

Polyurethanes (PUs) are thermoplastic polymers (some belong to the family of thermosetting polymers) with a wide range of applications, including adhesives, asphalt additives, upholstery foams, and many others. PUs are usually block copolymers with glassy, or "hard," and rubbery, or "soft," segments and are composed of a rigid (hard)[1–3] diisocyanate linked to polyether or polyester. The versatile behavior of PU is associated with the block structure and the thermodynamic incompatibility of the segments; this incompatibility induces microphase segregation of the segments into distinct domains.[4,5]

In the polymer industry, fillers play an important role because of their ability to modify the properties of a polymer. The effect of these interactions depends on the nature of the polymer, the concentration of the filler, and the particle size and morphology of the filler. Inorganic fillers, such as silica (and more recently, nanosilicas) and hybrid silicas, have been extensively used in polymer industries because of the capacity of these fillers to form hydrogen bonds with the polymer. There are basically two ways to generate a polymer-silica nanocomposite: mixing nanosilica with the polymer or mixing a silica precursor with the polymer. In the former approach, the simple blending of the nanofiller with the polymer

has some restrictions because nanofillers easily aggregate.[6–9] To avoid aggregation of the filler, one can use *in situ* synthesis of silica or of hybrid silica. The precursors are added during polymer synthesis[10–13] or to the finished polymer.[14–17] The unusual properties obtained through the use of nanoparticles are generally associated with the large surface-to-volume ratio of the filler; this ratio enables more numerous and stronger polymer-filler interactions. A common way to obtain nanosized silica is through the sol-gel process from starting materials of alkoxysilanes.[18] This process is well described in the literature, is easy to execute and gives good control over the particle size.

In PUs, the use of silica-based fillers has been investigated in several applications. For instance, the controlled synthesis of silicas with nanometric dimensions allowed the development of PU-hybrid silica composites with better coating properties in water-based emulsions,[12] or with better shape-memory effects.[19] The addition of hybrid silicas to PU has also improved the thermal stability and increased the hydrophobicity.[9,20] Hosgor et al. reported an increase in flame retardancy, modulus and hardness for hybrid silica-PU composites.[21] Athawale and Kulkarni observed that the addition of silica precursors during the polymer synthesis generated stronger polymer-silica interactions
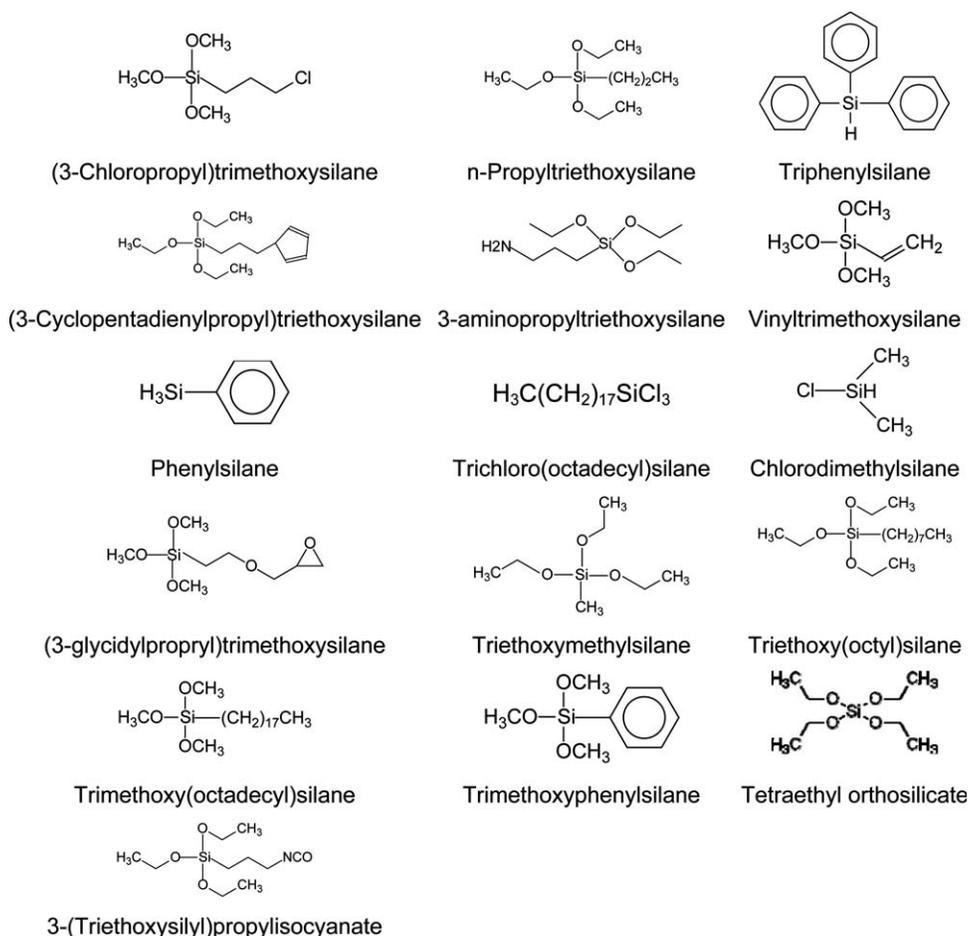
Scheme 1. Commercial organosilanes used.

than those obtained when silica was added after the polymer synthesis. These stronger interactions may confer better properties.[22] Similar behavior was reported by Kim et al., who observed an increase in hardness, initial modulus, and strength for tensile and compression loading. The shape fixity, shape recovery and strain energy storage increased, but the hysteresis loss was reduced.[23]

In spite of several examples of the use of silica on the modification of PU, to our knowledge, a systematic study does not exist in the literature concerning to the effect that the nature of organosilane has on the properties of PU. In this study, we report the effects of the *in situ* production of hybrid silica; the silica is produced by the sol-gel method and results from the combination of tetraethylorthosilicate (TEOS) with commercial organosilanes. Thirteen different organosilanes (see Scheme 1) have been employed. The choice of these compounds embraces differences in polarity and in the steric effects of the organic moieties. The resulting composites were characterized by SAXS, stress-strain test, and differential scanning calorimeter (DSC).

EXPERIMENTAL

Materials

Aqueous dispersions of PU (Dispercoll U54, gently donated by Bayer-50% w/w, $M_n = 34,000$ Da and $M_w = 169,000$ Da) was provided by the local adhesive industry. The organosilanes: (3-chloropropyl)trimethoxysilane, triethoxy(octyl)silane and vinyltrimethoxysilane from Dow (USA); 3-(triethoxysilyl)propylisocyanate, (3-glycidylpropyl)trimethoxysilane (98%), 3-aminopropyltriethoxysilane, phenylsilane (97%), triphenylsilane, trimethoxyphenylsilane, triethoxymethylsilane, *n*-propyltriethoxysilane, trimethoxy(octadecyl)silane from Sigma-Aldrich (Germany); chlorodimethylsilane and TEOS from Merck (Germany), trichloro(octadecyl)silane from Acros Organics (USA) and (3-cyclopentadienylpropyl)triethoxysilane from ABCR (Germany) were used as received.

Synthesis of PU-Hybrid Silica Films

First, water was removed from the PU emulsion by vacuum; then, the residual PU was redissolved in dichloromethane (ratio 1/25). TEOS was added under stirring to the organic PU solution in sufficient quantity to form 3 wt % SiO_2. Condensation reaction was initiated by adventitious water. After 1 h, the organosilane (corresponding to 10 mol % of SiO_2) was added. pH was kept constant for all studies. The resulting system was stirred for 24 h. Films were obtained in a glass mold by evaporating the solvent at room temperature for two days. For comparison, films were also prepared from pristine PU and from PU modified with TEOS only.

Characterization of PU-Hybrid Silica Films

The mechanical properties (stress-strain test) of the obtained films was evaluated in a universal testing machine (EMIC DL1000) in accordance with ASTM D412 with a traction speed of 50 mm/min. We used 5 specimens for each sample and the thickness of the synthesized films lain between 1.3 and 1.5 mm.

The synchrotron small angle X-ray scattering (SAXS) measurements were performed at the Brazilian Synchrotron Light Laboratory-LNLS (Campinas, Brazil) with a radiation wavelength of 1.488 nm, a silicon monochromator and a pinhole collimator. The samples were placed in a sealed stainless steel holder with Kapton[TM] tape. The results were corrected by using an empty cell as a reference. The CCD detector (MAR 160) was set at 1549.8 and 2245.7 mm from the sample. The images were converted to two-dimensional spectra using the software package FIT2D (European Synchrotron Radiation Facility, France). For the determination of the interface thickness we considered the electronic density gradient with a sigmoidal model and $\sigma = (-\text{slope}/4\pi^2)^{1/2}$.

The thermal properties of the compounds were evaluated with a DSC Model Q20 (TA Instruments). The measurements were performed under an inert atmosphere of nitrogen between -85 and $200°C$ at a heating rate of $10°C$ min^{-1}. The heating cycle was performed twice to eliminate the thermal history of the sample. In the determination of the parameters, only the second heating cycle was considered. The samples were taken from the obtained films.

Theoretical Calculations

The geometries of all species were obtained through full, unconstrained optimizations performed with density functional theory and the B3LYP hybrid functional obtained by the three parameter fit of the exchange-correlation potential suggested by Becke[24] and the gradient-corrected correlation functional of Lee et al.[25] in the DGDZVP basis set.[26–28] All calculations were performed with the Gaussian 03 program and used standard procedures and parameters.[29] The molecular volume was estimated for the lower energy structure by integration of the volume inside the surface with a density of 0.001 electrons/bohr[3]. The SPSS Statistical System (SPSS for Windows, version 19, IBM®) was used to perform the correlation analysis.

RESULTS

In the following presentation, the named organosilanes refer to the resulting PU film containing the hybrid silica. Thus, for instance, any allusion to the effect of triphenylsilane on the properties of a given PU film refers to the effect of the silica generated *in situ* with phenyl groups on its surface. For the *in situ* synthesis of the hybrid materials, the organosilane was deliberately added after 1 h of the start of the reaction (hydrolysis and condensation) with TEOS. This choice was made aiming at exposing the organic moieties on the uppermost external part of the formed silica particle; otherwise there was the risk of bearing such organic group within the formed silica structure, as already described in the literature.[30] Furthermore, the initial formation of the silica particles provide a support surface bearing silanol groups, which were capable to react further with

chloride, hydride, and alkoxyde groups from the organosilane, resulting therefore in the hybrid silica, as already discussed in the literature.[31] In the case of 3-(triethoxysilyl)propylisocyanate, one cannot neglect the possibility that isocyanate groups may hydrolyze in water to form amine, and then react with other isocyanate groups to form urea. Nevertheless, the hydrolysis of this material has not been observed under normal conditions, nor any special behavior has been observed particularly for this PU composite.

Stress-Strain Test

Figure 1 shows the mechanical properties obtained by stress tests of the PU-hybrid silica films. For better visualization, the results were divided into three groups: (i) films produced with hybrid silicas in which the organosilanes bear a propyl group [Figure 1(a)]; (ii) PU-hybrid silica films with organosilanes bearing alkyl groups [Figure 1(b)] and (iii) PU-hybrid silica produced with the remaining commercial organosilanes.

As shown in Figure 1, the films show a short elastic deformation followed by a plastic deformation; this is typical plastic behavior. From the curves illustrated in Figure 1, the yield stress, stress at break and elongation at break were extracted and are shown in Table I.

From Table I, the results showed that the *in situ* generation of hybrid silicas leads to a reduction of the mean yield stress and an increasing in terms of elongation at break, but mean the stress at break seem to be dependent on the nature of the organosilane. Apparently, the reduction on these mechanical properties may be resulting from phase separation of the resulting composite, as shown in Figure 2, which in turn may be a consequence of the resulting surface tension generated by the presence of the organic groups from the resulting hybrid silicas. It is worth mentioning that films with a large enough resistance for the mechanical tests could not be obtained for trichloro(octadecyl)silane and chlorodimethylsilane. This behavior may be due to the interactions PU-HCl, which is formed by hydrolysis of the chlorinated silanes. It is worth noting that no significant carbonyl stretching band shift has been observed for the systems by Fourier transform infrared (FTIR).

Thermal Analysis

Some typical thermograms obtained from DSC analysis are depicted in Figure 3. For the sake of better visualization, thermogramms ranging from -80 to $60°C$ are shown in two parts. These resulting thermal properties are presented in Table II. The presence of multiple endothermic processes in PU is a well-known and well-studied characteristic.[32–35] These processes are assigned to the internal rearrangement of hard domains. The samples had three thermal events: (i) the glass transition temperature (T_g) at $\sim -50°C$; (ii) an exothermic process (the crystallization temperature, T_c) at $\sim 5°C$; and (iii) two endothermic processes (melting temperatures, T_m) at $\sim 50°C$. For the pristine PU, the samples showed little variation in the T_g value. A small change in the T_g suggests that the interactions of the hybrid silica with the amorphous phase are small in intensity. A reduction in the ΔC_p in the region of T_g can also be observed and indicates that part of the amorphous phase may interact with the surfaces of the silica particles. The immobilization of the
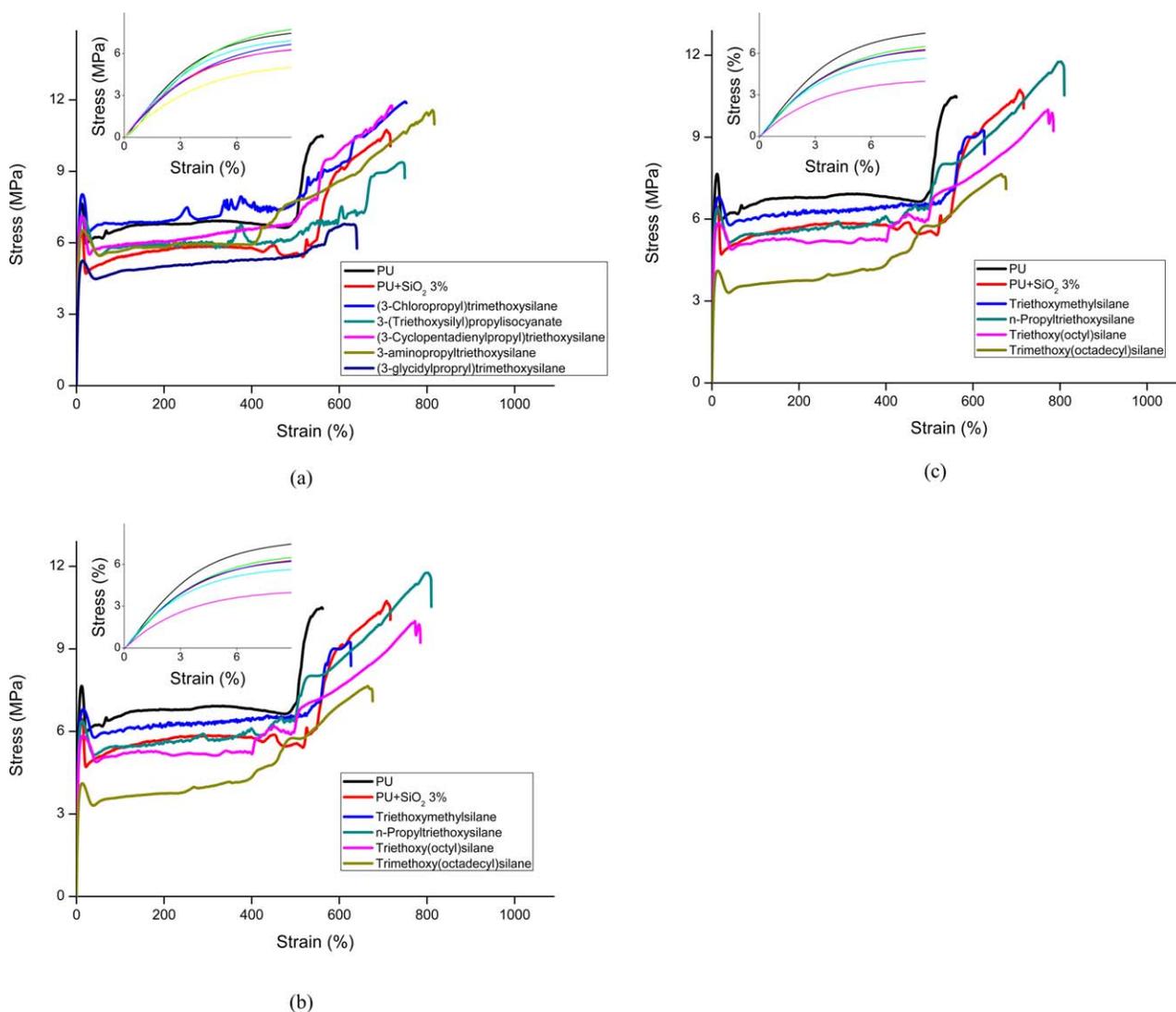
Figure 1. Mechanical properties of PU-hybrid silica films. (a) Organosilanes containing propyl groups; (b) organosilanes containing different alkyl groups; (c) Organosilanes containing different organic functional groups. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer chains by the hybrid silica reduces the mobility of such chains; therefore, this immobilization affects T_g. As shown in Table II, the results indicate that the generation of hybrid silica led to a reduction in the crystallization temperature relative to that of bare PU. The thermograms show a discrete T_g at $\sim -53°C$. The fusion of the hard domains takes place in two steps: one between 40 and 45°C and another one between 45 and 50°C. For trichloro(octadecyl)silane, these transitions occur between 35 and 40°C and between 40 and 45°C. In the crystallization process, samples with hybrid silica showed a decrease in the crystallization temperature; this result suggests that the hybrid silica retards the PU crystallization. The enthalpy of the crystallization process tended to decrease. In the melting process, the T_m also shifts towards lower values also. The presence of two peaks indicates that not all the hard domains have the same dimensions and possibly that the domains do not have the same degrees of order (arrangements). The behavior of the enthalpy of the melting process suggests that the generation of

hybrid silica in PU reduces the extent of the hard phase. The samples containing trichloro(octadecyl)silane and chlorodimethylsilane and (3-glycidylpropyl)trimethoxysilane showed a significant change in Tm. These samples, unlike the others, showed a temperature reduction for the melting process and an increase in the enthalpy of the process. Possibly, this effect is due to side reactions, since these organosilanes release hydrochloride acid when reacted with moisture. The enthalpy of the fusion process tended to decrease with the addition of hybrid silica. It is worth noting that these compounds can react with the PU, that is, parallel reactions may have taken place, like chlorinated silanes can produce HCl as by product, isocyanate silane can decompose and form urea.

Small Angle X-ray Scattering

The results of SAXS are illustrated in Figure 4 as the scattering intensity (I) as a function of the scattering vector (q), which is related to the scattering angle θ as $q = (4\pi/\lambda) \sin (\theta/2)$ where

Table I. Mechanical Properties of the PU-Hybrid Silica Films

Organosilane	Yield stress (MPa)	Stress at break (MPa)	Elongation at break (%)
(3-Chloropropyl)trimethoxysilane	7.9 ± 0.5	11.6 ± 0.5	751 ± 94
3-(Triethoxysilyl)propylisocyanate	7.3 ± 0.2	9.9 ± 1.1	724 ± 114
(3-Cyclopentadienylpropyl)triethoxysilane	6.9 ± 0.4	11 ± 0.6	705 ± 52
3-aminopropyltriethoxysilane	6.8 ± 0.2	12.4 ± 0.7	847 ± 90
(3-glycidylpropryl)trimethoxysilane	5.1 ± 0.5	6.7 ± 0.5	643 ± 123
Trimethoxyphenylsilane	7.3 ± 0.5	10.9 ± 0.5	776 ± 60
Vinyltrimethoxysilane	7.3 ± 0.6	14.4 ± 3.8	1010 ± 202
Trimethoxy(octadecyl)silane	4.2 ± 0.1	6.5 ± 1.4	619 ± 76
Triethoxy(octyl)silane	6.3 ± 0.4	10.6 ± 0.9	794 ± 30
n-Propyltriethoxysilane	6.4 ± 0.2	12.2 ± 0.8	805 ± 28
Triethoxymethylsilane	6.4 ± 0.4	8.8 ± 0.4	603 ± 40
Triphenylsilane	5.3 ± 0.2	13.3 ± 0.3	845 ± 48
Phenylsilane	7.0 ± 0.1	9.7 ± 1.2	690 ± 153
PU	7.8 ± 0.5	11 ± 0.9	592 ± 68
PU + SiO$_2$ (3 wt %)	7.1 ± 0.5	10.8 ± 0.7	815 ± 90

λ is the wavelength of incidence. As shown in the Figure 4, the samples present a peak, with the exception of the film containing triclorooctadecylsilane. The formation of peaks is characteristic of PU with a lamellar structure. From a qualitative perspective, well-defined narrow peaks are related to the extent of the arrangement of the hard domains whereas broad peaks indicate the formation of aggregates of a few lamellae.[4] If the phase separation were distributed randomly, the scattering curve would not present a maximum. After application of the Lorentz correction, the peak became better defined. The SAXS curves showed only one peak; this result indicates that the samples have a regular arrangement. The profile curves for the triclorooctadecilsilane sample, which showed a broad peak, indicate a lower spatial extent than that presented by other samples.

From the SAXS curves, one can obtain the interdomain spacing (d, the average distance between two hard domains),[4] the invariant Q [Q, which is related to phase segregation and is defined as $Q = \int I(q)q2\partial q$ (eq. (1)] and the interphase thickness (σ).[36] These results are presented in Table III.

The results show a small reduction in the domain spacing, an increase in the invariant Q (related to an increase in the degree of phase separation) and a tendency toward a reduction in the size of the interphase thicknesses between domains (σ). The results for the domain spacing and interphase thickness are close to those reported by other researchers[4,37–39] for PU films.

The samples with chlorine atoms directly bonded to the silicon atoms showed peaks significantly wider than the other samples. This peak broadening is because of the greater disorder in the structures. These same samples showed the greatest variation in the interdomain distance and had the highest phase separation (the invariant Q), which is consistent with a reduction in the degree of order.

Molecular Modeling

Table IV shows the volume of the organosilane group from the investigated organosilanes as calculated through molecular modeling. Figure 5 shows the correlation between the invariant Q and the calculated volume of the organic group of the hybrid silica. For the nonpolar organic groups, statistical analysis of the results shows a strong Pearson's correlation (0.758) between the measured invariant Q and the calculated volume of the organic group of the hybrid silica.

DISCUSSION

The observed increase in the phase segregation with the increase in the calculated volume of the organic groups is possibly because of a reduction in the interaction between the silica and the hard domains. This reduction occurs because the addition of nonpolar organic groups to the hybrid silica surface increases the distance between the OH groups on the silica surface and the polar groups in the hard domains in PU.

Statistical analysis of the results also shows a strong PearsonÇs correlation between the yield stress and T_g (−0.62), the yield stress and T_m (0.74), the stress at break and the elongation at break (0.70), the T_g and the interdomain spacing (−0.68), and the interphase thickness and the domain spacing (0.73). These correlation factors show that the variation in properties is in accordance with the concepts of polymer theory.

Upon an initial examination, one can conclude that the *in situ* generation of hybrid silica in PU improves the stress at break. A reduction in the yield stress was obtained with the addition of hybrid silica. This parameter (the yield stress) often limits the use of the polymer because after this stress, the polymer does not return to its original dimensions. In pure PU, this limit is determined by the hard domains and the interactions of the hard domains with the amorphous phase. The hard domains act as cross-linking points and limit the movements of the
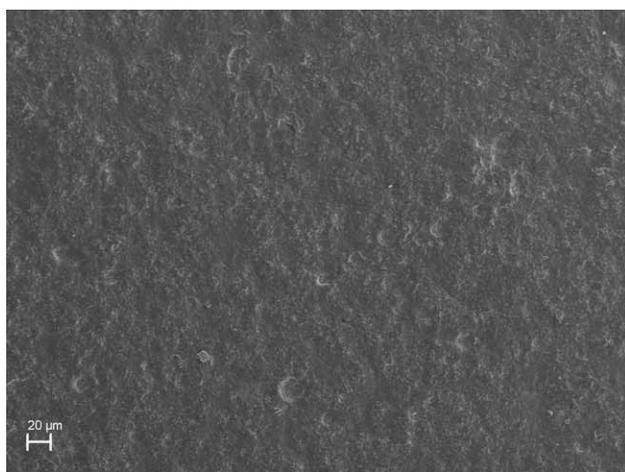
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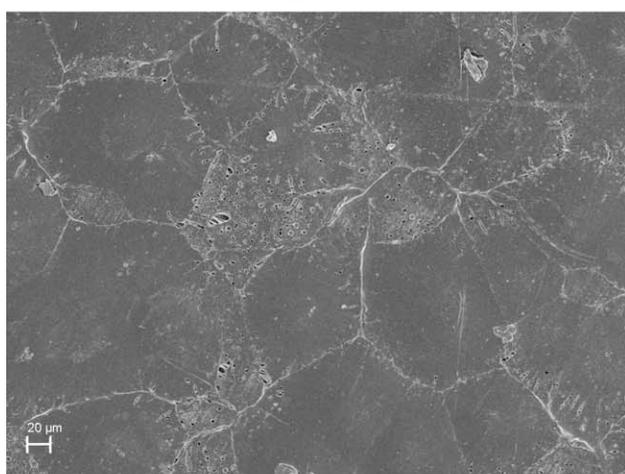
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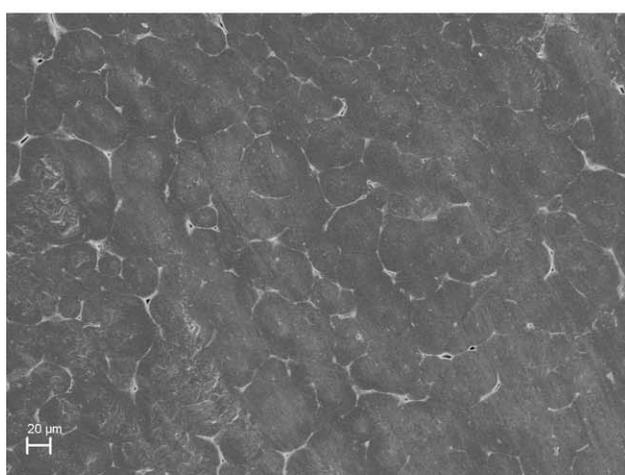
(c)

Figure 2. Micrographis of the resulting composite PU and (a) TEOS; (b) 3-(triethoxysilyl)propylisocyanate; and (c) vinyltrimethoxysilane.

chains of the amorphous phase. The transition zone phase also affects this behavior. Smaller dimensions for transition zone phases imply that the phase separation is higher and

consequently, that there are smaller interactions between phases. This fact is observed because the mobility of the chains of the amorphous phase increases. Comparing the values for the yield stress with the values for the invariant Q, one can conclude that an increase in phase separation is inversely proportional to the yield stress. One must consider that the phase separation is not the only factor that determines the magnitude of the yield stress. The interaction of the silica-bearing organic groups with the amorphous phase and the degree of aggregation of the silica also contributes.

The results show that the substitution of silanol groups on the silica surface by alkyl groups has a trend associated with the length of the alkyl group. Groups with one to three carbons exhibit very similar results. The results suggest that an increase in the chain length of organosilane (n-octyltriethoxysilane and octadecyltrimethoxysilane) increases the mobility of the chains of the amorphous phase. The samples with trichlorooctadecylsilane and chlorodimethylsilane showed different behaviors. The resistance of the samples was so reduced that it was not possible to obtain a film resistant enough for a stress-strain test. Based on the SAXS measurements, both samples showed a
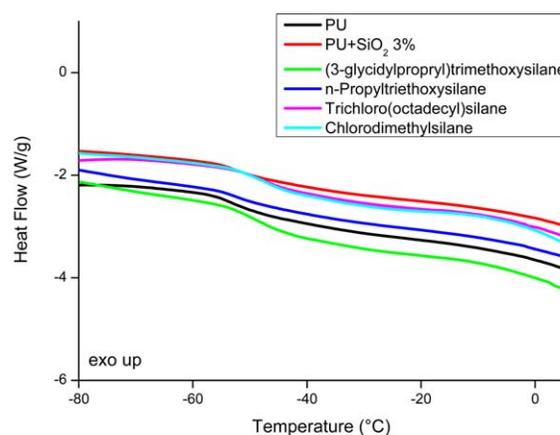
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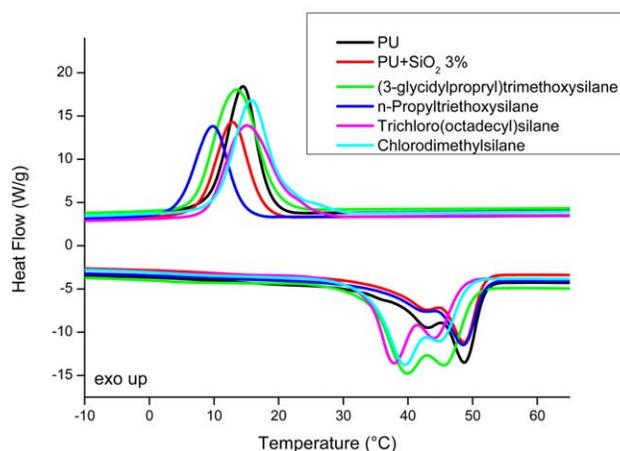
(b)

Figure 3. Examples of typical thermograms for PU-hybrid silica films. (a) T_g region and (b) T_m region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Thermal Properties of the PU-Hybrid Silica Films

| Organosilane	T_g (°C)	ΔC_p (°C J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})
(3-Chloropropyl)trimethoxysilane	−52	0.28	49	48.2	12	44.5
3-(Triethoxysilyl)propylisocyanate	−54	0.31	49	51.0	12	46.5
(3-Cyclopentadienylpropyl)triethoxysilane	−53	0.30	48	42.2	9	43.2
3-Aminopropyltriethoxysilane	−53	0.20	49	41.3	10	43.2
(3-Glycidylpropryl)trimethoxysilane	−49	0.27	40	54.5	14	52.2
Trimethoxyphenylsilane	−53	0.28	48	49.4	10	45.9
Vinyltrimethoxysilane	−53	0.26	49	45.2	9	44.1
Trichloro(octadecyl)silane	−49	0.38	38	52.7	15	52.2
Chlorodimethylsilane	−47	0.35	40	50.9	16	50.7
Trimethoxy(octadecyl)silane	−51	0.28	49	47.7	4	45.0
Triethoxy(octyl)silane	−53	0.35	48	48.6	11	50.3
n-Propyltriethoxysilane	−52	0.20	49	43.3	10	44.3
Triethoxymethylsilane	−52	0.25	49	45.6	9	46.0
Triphenylsilane	−53	0.19	49	44.1	11	46.3
Phenylsilane	−52	0.24	48	45.2	7	43.3
PU	−53	0.33	49	44.2	15	47.6
PU + SiO$_2$ (3 wt %)	−52	0.29	49	42.0	13	44.8

considerable increase in the phase separation; this result may explain the loss of strength in these samples. Using 3-aminopropyltriethoxysilane, Xiaojuan et al.[40] assign the observed changes in the mechanical properties to the crosslinking of the polymer with the hybrid silica. In this study, no evidence of crosslinking could be observed.

The DSC results in the Tc region showed a tendency toward a reduction in the T_c whereas the enthalpy does not show a clear trend. This behavior is most likely because of the process in solution, which does not favor nucleation and therefore tends to form smaller crystals. Only the samples trichloro(octadecyl)-silane, chlorodimethylsilane and (3-glycidylpropyl)trimethoxysilane showed an increase in T_c and in the enthalpy of the process; this result is most likely also because of reactions between the hybrid silica and the PU. The T_g showed a tendency to increase and showed an increase of up to 5°C, which is a small variation for a high molecular weight polymer. This increase in T_g may be associated with the immobilization of the chains on the silica surface. The variation of the specific heat at constant pressure (ΔC_p) was reduced in the range of the T_g; this result indicates that some of the chains of the amorphous phase are immobilized on the silica surface, as described by Lipatov.[41] Pristine PU showed a endothermic transition with a clear shoulder at 48°C. With the generation of hybrid silica, these transitions slightly shifted to lower temperatures, and the enthalpy of the process was reduced. This suggests that the crystallinity is reduced. The samples with trichloro(octadecyl)silane, chlorodimethylsilane and (3-glycidylpropyl)trimethoxysilane showed the greatest variation in Tm but had an increased enthalpy for the process; this increased enthalpy most likely resulted from reactions between the hybrid silica and the PU. It is worth noting that among PU-hybrid films containing propyl

groups in the organosilane moieties, those films containing (3-glycidylpropyl) groups exhibited the lowest stress at break. Such samples showed the lowest mechanical properties among all the samples. When we compared the results obtained by DSC (Figure 3), the increasing in melting enthalpy indicates a significant change in crystallinity. It is also observed that the melting temperature (Tm) is shifted to lower temperatures. These DSC results are closer to those obtained with trichloro(octadecyl)si-lane and chlorodimethylsilane samples, suggesting that interactions in (3-glycidylpropyl)trimethoxysilane-PU causes a break in the extension of the ordering of the hard segments.

As previously mentioned, the occurrence of multiple endothermic processes in PU is described in the literature. These
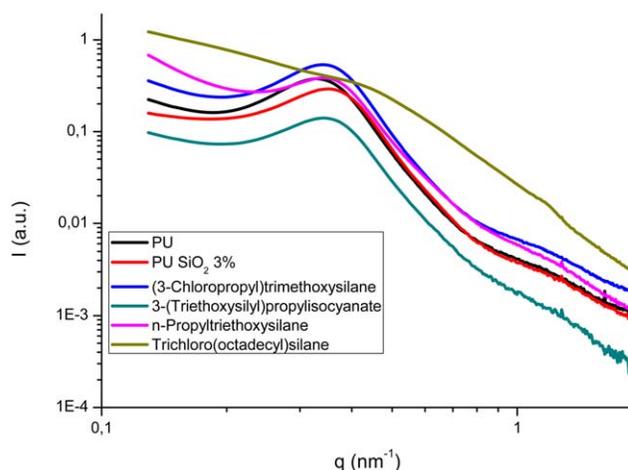
Figure 4. Typical SAXS curves for PU-hybrid silica films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Parameters Extracted from SAXS Curves

Organosilane	d^a (nm)	Invariant Q (a.u.)	σ^b (nm)
(3-Chloropropyl)trimethoxysilane	17.4	1.93×10^{-2}	0.20
3-(Triethoxysilyl)propylisocyanate	16.8	5.76×10^{-3}	0.26
(3-Cyclopentadienylpropyl)triethoxysilane	17.1	2.17×10^{-2}	0.21
3-Aminopropyltriethoxysilane	17.1	2.45×10^{-2}	0.10
(3-Glycidylpropryl)trimethoxysilane	17.4	1.73×10^{-2}	0.25
Trimethoxyphenylsilane	16.8	2.52×10^{-3}	0.14
Vinyltrimethoxysilane	16.8	1.31×10^{-2}	0.19
Trichloro(octadecyl)silane	13.9	4.96×10^{-2}	0.09
Chlorodimethylsilane	14.3	3.15×10^{-2}	0.07
Trimethoxy(octadecyl)silane	17.4	2.65×10^{-2}	0.30
Triethoxy(octyl)silane	17.1	1.75×10^{-2}	0.29
n-Propyltriethoxysilane	17.1	1.79×10^{-2}	0.23
Triethoxymethylsilane	17.7	1.51×10^{-2}	0.26
Triphenylsilane	17.1	2.06×10^{-2}	0.22
Phenylsilane	17.1	3.10×10^{-3}	0.22
PU	17.7	1.37×10^{-2}	0.26
PU + SiO$_2$ (3 wt %)	16.8	1.26×10^{-2}	0.24

^{a} Interdomain spacing.
^{b} Interphase thickness.

multiple endothermic processes are attributed to internal rearrangement of the hard domains.[32,42–46] While studying the addition of various amounts of silica with silanol groups to PU prepared in a laboratory, Vega-Baudrit et al.[47] observed an increase in phase separation. In their work, a reduction in T_g was also reported with lower levels of silanol groups. In their work, Petrovic et al.[42] observed that the endothermic processes shifted to higher temperatures as the silica content increased and attributed this behavior to the change in morphology. From X-ray diffraction studies, the authors concluded that the addition of silica reduces the crystallization of the hard segments. The same authors also observed that interactions between the polymer phases are stronger than those of the silica/amorphous phase and that the addition of silica increases the free volume of the polymer matrix.

Chen et al.[48] suggested that the use of organic groups, which form a dense layer on the silica surface, reduces the tendency of the silica particles to aggregate. The same authors suggested that the use of unsaturated organic groups allows chemical bonds to form between the silica and the polymer. This behavior was not observed in our study. In another report,[49] Chen et al. allege that the variations in PU properties are only attained with small amounts of nanosized silica. At higher concentrations (generally above 10%), the properties are because of polymer-silica charge interactions.

Because T_g is inversely proportional to the mobility of amorphous segments, the increase in T_g for the samples containing trichloro(octadecyl)silane, chlorodimethylsilane and (3-glycidylpropryl)trimethoxysilane suggests that interactions are stronger and the mobility of the amorphous segments is reduced.

Likewise, these results indicate a reduction in the degree of order, as demonstrated by the observed increase of T_c. The shift of Tm to lower temperatures and the increase in the enthalpy of the process showed that mobility is reduced through limits of the extent of spatial ordering.

Vega-Baudrit et al.[47] described the variation in the degree of phase separation caused by the interactions of the silanol groups

Table IV. Calculated Volume of the Organic Radicals Used in the Hybrid Silica Synthesis

Organosilane	Volume (cm^3 mol^{-1})
(3-Chloropropyl)trimethoxysilane	166.1
3-(Triethoxysilyl)propylisocyanate	188.1
(3-Cyclopentadienylpropyl)triethoxysilane	239.2
3-Aminopropyltriethoxysilane	178.7
(3-Glycidylpropryl)trimethoxysilane	169.3
Trimethoxyphenylsilane	156.2
Vinyltrimethoxysilane	124.7
Trimethoxy(octadecyl)silane	354.0
Triethoxy(octyl)silane	261.6
n-Propyltriethoxysilane	158.0
Triethoxymethylsilane	138.9
Triphenylsilane	204.7
Trichloro(octadecyl)silane	343.0
Chlorodimethylsilane	84.4
Phenylsilane	89.2
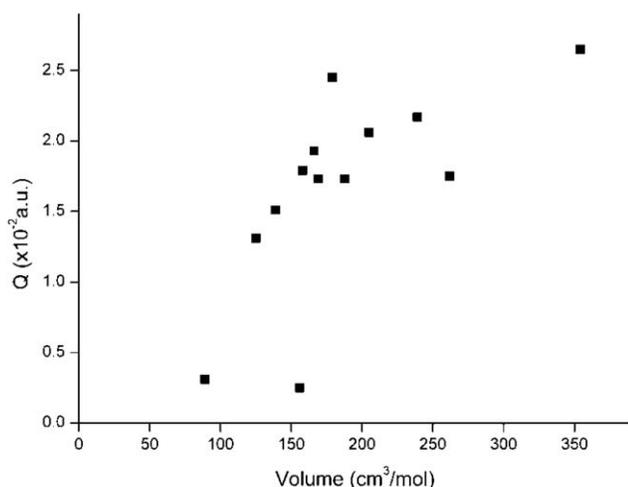
Figure 5. Correlation between the invariant Q and the calculated volume of the organic group of the hybrid silica.

with the carbonyls of PU and detected by FTIR. These polymer-silica interactions reduce the interactions between the polymer phases and increase the phase separation; in turn, this increase leads to a reduction in the mechanical properties. These authors also reported that silanol-carbonyl interactions are weaker than NH-carbonyl interactions, and this increased weakness increases the mobility of the chains of the amorphous phase and provides greater ordering in this phase. In our samples, no alteration in the carbonyl absorption wavenumber shift could be observed by FTIR. The same authors also reported a reduction in the T_g of the amorphous phase, but this variation is not linear with the concentration of silanol groups. The authors also described competing effects that are also associated with the degree of aggregation of the silica.

In our work, the variation of the properties of the PU obtained by generating silica and hybrid silica (with polar organic groups) *in situ* was lower than expected. These results suggest that the addition of silica reduces the interactions between the polymer phase and that the silica-polymer interactions are weaker than those between the polymer phases. When a filler is added to promote a reinforcing effect, that is, to improve the mechanical properties, the polymer layer must be immobilized in contact with the surface of the filler. The obtained reduction in the TLE is consistent if one assumes that the silica-polymer interactions are weaker than the interactions between the hard and amorphous phases of the polymer.

The results showed that, under the studied conditions, the addition of hybrid silica did not result in an improvement in mechanical properties. The observed increases in the stress and elongation at break is consistent with the behavior described in the literature, that is, the interactions between two or more hard segments are stronger than those between the hard domains and the chains of the amorphous phase.[35,47] In the plastic deformation zone, the hard domains align because of the interactions between the domains, and this alignment ultimately provides resistance to deformation.

CONCLUSIONS

The results showed that addition of hybrid silica increases the phase separation of the PU. The results also suggest that the interactions between hybrid silica and the polymer chains are weak. The results show that the *in situ* generation of silica or hybrid silica in PU led to a reduction in the crystallization temperature and indicate that no nucleation processes were induced by the addition of hybrid silica.

Comparing the results from SAXS and DSC, one observes that the addition of hybrid silicas disturbs the hard domains. These domains act as hard crosslinking points and eventually cause a reduction in the "melting" temperature of these domains. One cannot neglect that thixotropy depends on the silica surface hydrophobicity, and such analysis demands further studies. Based on the set of investigated organosilanes, the results showed that the steric effects of the organic moieties were more relevant to the effects observed in the resulting PU composites than the natures of the organic groups.

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