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Using the Nanostructure of Segmented Polyurethanes as a Template in the Fabrication of Nanocomposites

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The ability to have different types of molecular architectures specifically designed for each application has made polyurethanes (PUs) one of the most popular polymers used in a variety of products, such as coatings, adhesives, flexible and rigid foams, elastomers, tough solids, among others.[1] On the other hand, novel and more advanced applications for polyurethanes (such as in optoelectronics, food, and biomedical fields) that involve either specificity or tailorable properties require special novel well-controlled structures and functionalities. In this work, inorganic species were incorporated into polyurethanes having different macromolecular architectures to produce a series of nanostructured composites. Inorganic functionalities can have a range of roles, when controlled, distributed, and organized within a polymer network: (a) sites for chemical reactions to proceed;[2] (b) sites for biomacromolecules immobilization;[3] (c) sites for molecular breakdown and biodegradation;[4] among others.

The idea of this work was to explore the special self-assembly nanostructure developed by segmented polyurethanes by using it as a template in the preparation of nanocomposites. More recently, block copolymers have been modified with inorganic precursors to produce well-organized nanocomposites having a range of phase morphologies.[5,6] In this work, inorganic moieties were incorporated into polyurethanes having different segmented chain configurations to yield a variety of nanostructured materials. Inorganic functionalities, based on Si−O bonds, were attached to the hard segments of a series of polyurethanes containing different hard to soft segment ratios to produce structurally tailored networks that would take advantage of the self-assembly capacity of the polymer to control the organization of inorganic entities.

A series of aliphatic polyurethanes were synthesized with different hard to soft segment ratios by reacting polyether diols (M_n = 1000 g/mol) and isophoreno diisocyanate (IPDI) in proportions to yield isocianate (NCO) to hydroxyl (OH) equivalent ratios ranging from 1.5 to 3.0. Isocyanate-terminated chains were then reacted with (aminopropyl)triethoxysilane (APTS) to produce triethoxyxysilane end-capped chains. After that, deionized water (pH = 5.0, water to APTS molar ratio = 5) was added to the mixture in order to hydrolyze the APTS alkoxy groups. Table 1 reports the weight percent of each reagent used to produce the different polyurethanes and the theoretical inorganic content incorporated into them, assuming that all silane molecules were converted into inorganic siloxane bonds. Table 1 also exhibited the theoretical proportion of hard segments of the modified PU. These values were calculated by assuming that the inorganic species based on APTS were incorporated into the hard segments derived from IPDI.

Table 1. Weight Percent of Reagents Used To Produce Pure Polyurethanes (PU) and Polyurethanes Modified with Inorganic Species (HB)

sample	polyol (wt %)	IPDI (wt %)	APTS (wt %)	theor SiO_2 content (wt %)[a]	theor hard segment content (wt %)[b]
PU-A	81.74	18.26	0		18.26
PU-B	77.04	22.96	0		22.96
PU-C	72.86	27.14	0		27.14
PU-D	69.11	30.89	0		30.89
HB-A	73.24	16.36	10.39	3.01	24.80
HB-B	62.89	18.74	18.37	5.75	34.08
HB-C	55.66	20.73	23.61	7.75	40.85
HB-D	49.01	21.91	29.08	9.99	47.14

[a] Theoretical wt % of SiO_2 calculated assuming that 221 g of APTS produce 60 g of SiO_2. [b] APTS + IPDI. Assuming that 75% of the alkoxy groups in APTS turned into Si−O−Si units.

Representative synchrotron small-angle X-ray scattering (SAXS) data as a function of the scattering vector (q) for polyurethanes having different hard to soft segment ratios are shown in Figure 1. It is possible to observe that a small and wide scattering peak becomes more pronounced as the concentration of the hard segments is increased. The presence of scattering peaks within SAXS data is usually interpreted as a consequence of the presence of distinct microphases with more defined and different electron densities.[7−9] Therefore, data in Figure 1 indicate that higher contents of hard segments in polyurethanes led to the production of polymers with more well-defined microphase-separated structures. The presence of higher contents of hard segments is also capable of allowing the formation of higher concentrations of hydrogen bonds between amine and carbonyl groups located at the hard segments that can emphasize phase incompatibility. This result was correlated with FTIR results that suggested that the amount of hydrogen bond increases as the concentration of hard segments is enhanced in the polymer.

The position of the scattering peaks in SAXS intensity profiles can be related to the interdomain repeat distance (L), defined as the average distance between two hard domains composed of polyurethane hard segments, by applying Bragg's equation.[7,9,10] In Figure 1, it is evident that the scattering peaks tend to shift toward lower values of scattering vector as the amount of hard segments is increased in the systems. Lower values of q of the peaks mean larger distances between hard domains (L). This result can be understood by considering that both morphology and dimensions of the microphases can play a role in defining sizes within the nanostructure. The effect of the content of the phases in microphase-separated systems on the morphology is quite known, particularly for block copolymers.[6] Beyond changes in morphology, the degree of compatibility and the size of the domains can also change as a function of the composition and can contribute to the observed values of L. Compatibility seems to decrease as the content of hard segment is enhanced, as indicated by scattering data and FTIR results. Lower levels of

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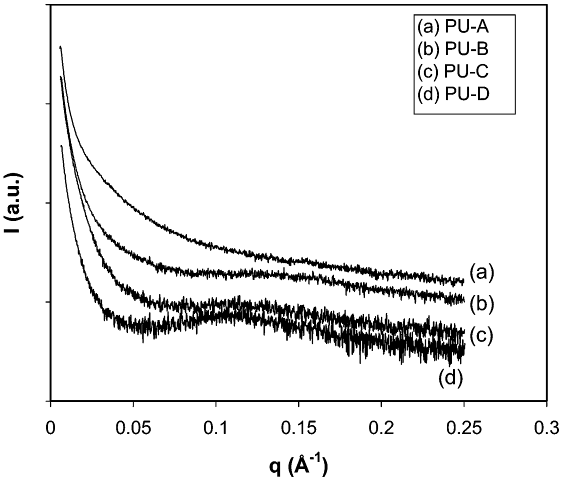

Figure 1. SAXS curves for pure polyurethanes. The curves were moved in the *y* direction for clarity.

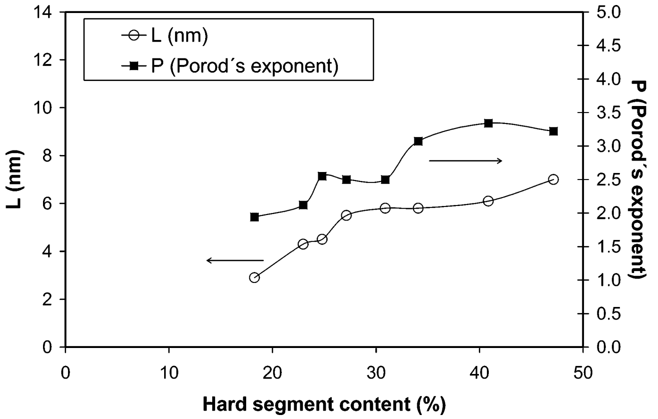

Figure 2. Effect of hard segment content on structural parameters derived from SAXS data: *L* (interdomain repeat distance) and *P* (Porod's power-law exponent).

compatibility can lead to phases with more well-defined compositions and interfaces and higher densities. Higher mobility of the pre-polyurethane chains combined with lower compatibility between phases can favor the coarsening of the phases and, consequently, chain stretching.[8] Values of *L* for the different polyurethanes are presented in Figure 2.

SAXS intensity profiles for polyurethanes having different contents of inorganic species attached to PU hard segments are shown in Figure 3. The presence of wide scattering peaks in SAXS curves is again evidence that a microphase-separated structure is present within inorganic modified segmented PU. The comparison between SAXS patterns of polyurethane with inorganic species (Figure 3) and their counterpart pure polyurethanes (Figure 1) reveals that scattering peaks become more intense, wider, and located at lower values of scattering vector (q) as inorganic species were incorporated into PU, as an indication that phase separation becomes more pronounced as the inorganic species are introduced in polyurethane network. Increase in intensity of the scattering peak means that formed microphases have higher differences in electron density that suggest higher densities and better defined interfaces. The values of the long spacing *L* parameter for these modified polyurethanes are reported in Figure 2. The overall result showed that there is a steadily increase in *L* as the content of hard segments is enhanced in PU by either increasing the NCO/OH ratios

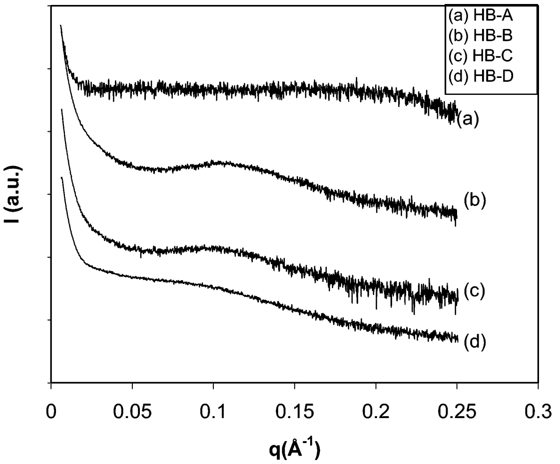

Figure 3. SAXS curves for polyurethanes modified with inorganic species. The curves were moved in the *y* direction for clarity.

during prepolymer preparation or by inserting inorganic groups at prepolymer chain ends. The fact that the *L* values progressively increase as a function of the content of hard segment (Figure 2), regardless of whether the hard segment is composed only with urethane/urea bonds or composed of both urethane/urea bonds and inorganic species, suggests that, in polyurethanes modified with inorganic species, these species are being confined within hard domains instead of, for example, being consumed in the creation of new types of nanostructure containing a variety of different types of domains. DSC results also confirm this last hypothesis, since no alteration in T_g of the soft segments was observed when larger amounts of inorganic species were added. Impregnation of inorganic species within soft segments would result in an increase in T_g of the soft segments. FTIR results showed also that more hydrogen-bonded carbonyl groups are present in inorganic modified PU's, as evidence that the demixing between hard and soft segments becomes more pronounced.

It is reasonable to think that the incorporation of inorganic species, as was done in this work, did not disrupt the natural structural evolution of the segmented polyurethanes that occurs when the proportion of urethane/urea hard segments is increased in polyurethanes. Therefore, changes in morphology due to the increase in hard to soft segment ratios, obtained by adding inorganic species, should also follow the usual phase diagram of block copolymers and segmented polymers. The fact that *L* increases as the proportion of hard segments is raised in polyurethanes indicates that not only morphology but also dimensions of the microphase-separated structure change when inorganic species and urethane/urea bonds are incorporated in larger extensions in the material.

SAXS data were further explored by obtaining the Porod's power-law exponent (*P*) by extracting the slope of log−log intensity plots. The obtained values of *P* for all polyurethanes are depicted in Figure 2. The results showed that there is a gradual increase in *P* as the contents of hard segments are enhanced in PU. *P* values can be related to the fractal dimensions of the scattering bodies. Low values of *P* (between 1 and 3) are typical of mass fractal structures that can be described as being formed by noncompact aggregates, having low density and less defined surfaces.[11,12] Low values of *P* have been also related to less defined phase-separated structures.[13]

For PU having higher hard segment contents, *P* values approach 4, suggesting a progressive change in the fractal structure of the scattering bodies from mass fractal to surface fractal to smooth surfaces (for *P* values closer to 4) as the hard to soft segment ratio of the polyurethanes is enhanced (either by incorporating larger amounts of urethane/urea bonds or by incorporating inorganic species). Thus, polyurethanes having higher contents of hard segments may have a structure containing hard domains with more defined surfaces and densely packed networks.

The structural investigation, performed in polyurethanes having macromolecular architectures modified by inserting inorganic entities, was accomplished in this work. Major results showed that the microphase separation process in pure polyurethane is reproduced in PU modified with inorganic species. Inorganic entities, incorporated through the use of end-capped PU prepolymers, were mainly concentrated into hard domains, and these modified hard domains seem to resemble structurally hard domains of pure polyurethane. Structural parameters, obtained from mathematical manipulation of SAXS data, showed that hard domains in PU with higher concentration of hard segments and inorganic species have better defined interfaces, packed structures, and longer interdomain repeat distances. These results can suggest that the natural self-assembly and well-controlled nanostructures of segmented polyurethanes can be used as a template in the construction of nanocomposites (containing inorganic species) having defined structures that can be used in the fabrication of advanced devices that require higher levels of specificity and control such as biosensors, biomaterials, electrooptical devices, and others.

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