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Attachment of Inorganic Moieties Onto Aliphatic Polyurethanes

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Polyurethanes have been used in a series of applications due basically to their versatility in terms of controlling the behavior by altering basically the type of reagents used. However, for more specific and advanced applications, such as in membranes, biomaterials and sensors, well-organized and defined chemical functionalities are necessary. In this work, inorganic functionalities were incorporated into aliphatic polyurethanes (PU) having different macromolecular architectures. Polyurethanes were synthesized using a polyether diol and dicyclohexylmethane 4,4' diisocyanate (H_{12}-MDI). Polyurethanes having carboxylic acid groups were also produced by introducing 2,2- bis (hydroxymethyl) propionic acid in the polymerization process. Inorganic functionalities were inserted into polyurethanes by reacting isocyanate end capped chains with aminopropyltriethoxysilane followed by tetraethoxysilane. PU having carboxylic acid groups yielded transparent samples after the incorporation of inorganic entities, as an evidence of smaller and better dispersed inorganic entities in the polymer network. FTIR and swelling measurements showed that polyurethanes having carboxylic acid groups had inorganic domains less packed, condensed and cross-linked when compared to polyurethanes with no carboxylic acid groups. Results also suggested that the progressive incorporation of inorganic moieties in both types of polyurethanes occurred in regions previously activated with inorganic functionalities, instead of by the creation of new domains. The temperatures of thermal decomposition and glass transition were also shifted to higher temperatures when inorganic functionalities were incorporated into polyurethanes.

Keywords: *polyurethane, nanocomposites, inorganic groups*

1. Introduction

Polyurethanes (PUs) are polymers typically produced through the reaction between diisocyanates and polyols. Many different types of molecular architectures, that yield a variety of products, can be formed by selecting appropriate reagents. In aliphatic PUs, for example, which are based on aliphatic diisocyanates, their good weatherability has led to applications of this PU, such as coatings, adhesives, flexible foams, among others[1-3].

However, special applications (such as in optoelectronics, food and biomedical fields) that involve either extreme specificity or tailorable properties require special controlled structures. In this work, inorganic species and polyurethanes were organized into molecularly tailored structures in order to produce materials with tunable mechanical, physical and chemical properties. Inorganic functionalities can have a range of roles when controlled distributed and organized within a polymer network: a) sites for chemical reactions to proceed[4,5]; b) sites for biomacromolecules immobilization[6,7]; c) sites for molecular breakdown and biodegradation[8,9]; among others.

Association between polymers and inorganic species has been employed in many systems and in a variety of dimensional scales in order to produce high-performance composites. The association between stiff and strong ceramic fibers (as glass, carbon, boron fibers) with the inherent ductility and toughness of some polymers enables the fabrication of microcomposites with enhanced mechanical properties. On the other hand, a more pronounced integration between these different types of materials would be necessary to explore and exhaust their intrinsic chemical and physical potentialities. Several methods have been proposed and used to enable the preparation of polymers containing inorganic species distributed in a nano or molecular scale, for example: 1) incorporation of nano-layered silicate particles by using special delaminated clay minerals as additives in polymers[10-12]; 2) formation of nanoparticles of semi-conductors within polymers to produce opto-electronic devices[13]; 3) production of inorganic oxide particles within polymer matrices based on the sol-gel process to yield the so called "organic-inorganic hybrids"[14-16]; etc.

In this work, inorganic functionalities based on Si-O bonds were incorporated into polyurethanes to produce structurally designed networks having controlled presence of inorganic entities. This type of structurally designed materials may display controlled properties suitable for a series of important proposed applications, such as: high performance coatings and foams with enhanced mechanical properties; films and membrane with tunable permeabilities; biomaterials with specific sites for protein immobilization or drug impregnation; among others. The inorganic modified polymers were prepared by firstly activating aliphatic polyurethanes by end capping chains with siloxane groups. Subsequently, these groups were used as nucleation sites for the creation of inorganic domains through the reaction with tetraethoxysilane.

2. Experimental Procedure

2.1. Materials

POLY-G 55-112 (polyether diol, $M_n = 1000\ g.mol^{-1}$) and POLY-G 76-635 (polyether triol, $M_n = 265\ g.mol^{-1}$) were provided by Arch Chemicals, Inc. (Brazil). Dicyclohexylmethane 4,4' diisocyanate (H_{12}-MDI) was obtained from Bayer AG (Brazil). Aminopropyltriethoxysilane (APTS) and LIOCAT-118 (dibutyl tin dilaurate) were obtained from Degussa and Miracema Nuodex respectively. All these chemicals were employed throughout this work as received. Tetraethoxysilane (TEOS, Aldrich), dimethyl formamide (DMF, 99%

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Aldrich), 2,2- bis (hydroxymethyl) propionic acid (DMPA, 98.3%, Fluka) were purchased and also used as received.

2.2. Synthesis of inorganic modified PU

2.2.1. Preparation of pure polyurethanes (prepolymers PU)

Aliphatic polyurethanes with two different molecular architectures were synthesized and used as matrix for inorganic group attachment. Typically, in order to prepare the first type of polyurethane (PU-1), 49.79 g of Poly-G 55-112 and 0.99 g of Poly-G 678-35 were charged in a three-necked reaction vessel equipped with a mechanical stirrer and dissolved in 20 g of DMF solvent. Then, 29.21 g of H_{12}-MDI was added to prepare a PU at an equivalent ratio [NCO]/[OH] of 2:1 followed by addition of catalyst Liocat 118 (0.01 g). The reaction was carried out at 80 °C for 2 hours under nitrogen atmosphere. The concentration of [NCO] groups was determined by reacting the pre-polymer with excess dibutylamine and titrating the unreacted dibutylamine with HCl. The final concentration of PU in DMF was 80% by weight.

A second type of polyurethane (PU-2), containing carboxylic acid groups, was also prepared. Typically, 32.82 g of Poly-G 55-112, 1.24 g of Poly-G 678-35 and 4.05 g of DMPA were dissolved in 25 g of DMF solvent to form a 75 wt. (%) solution. The mixture was stirred under nitrogen for 30 minutes at 60 °C until total dissolution of the DMPA. Then, 36.87 g of H_{12}-MDI to prepare a pre-polymer with an equivalent ratio [NCO]/[OH] of 2:1 and the catalyst Liocat 118 (0.02 g) were added and the whole solution was heated to 100 °C for 2 hours.

2.2.2. Preparation of polyurethanes containing inorganic moieties

PU-1 polyurethane was firstly activated to be able to accommodate inorganic species. Chemical activation was performed by reacting PU-1 with aminopropyltriethoxysilane (APTS) in proportions to yield siloxane endcapped polyurethane chains (all isocyanate – NCO groups – end-capped by APTS). Suitable amounts of PU-1 prepolymer were mixed with DMF to form a 20 wt. (%) solution. At room temperature, APTS was added to the PU-1 solution to incorporate inorganic functionalities to PU-1. The mixture was stirred until the infrared absorption band relative to the isocyanate group (2200 cm^{-1}) of samples, periodically taken from the reaction vessel, disappeared. PU-1 containing inorganic functionalities was then reacted with hydrolyzed TEOS (hTEOS) to yield polymer having inorganic domains with designed structures (C1). For the acidic hydrolysis, TEOS and water (pH 1.5 with HCl 1N) at a molar ratio $[H_2O]/[TEOS]$ of 4:1 were stirred at room temperature for 40 minutes until the mixture was completely homogeneous. Different amounts of hTEOS (Table 1) were introduced into the solution containing PU-1 with siloxane endcapped groups to produce different types of inorganic modified polymers. The solution was then cast in polyethylene recipients that remained closed for one week at room temperature. After that, the recipients were opened and the inorganic modified polymer network was further polymerized at room temperature for 3 days and postcured at 60 °C for 24 hours. Table 1 reports the amount of TEOS introduced into the reaction vessel to produce polyurethanes with different inorganic contents. Table 1 also shows the theoretical inorganic content incorporated into polyurethanes, assuming that all silane molecules were converted into siloxane bonds.

Polyurethanes having carboxylic acid groups (PU-2) were also modified with inorganic entities by following a chemical procedure similar to the one described and used to produce the C1 materials. The main difference between procedures was associated with the fact that PU-2 samples containing inorganic functionalities (C2) were prepared by using TEOS without previous hydrolysis. APTS was again used to activate the polyurethane to be able to incorporate inorganic functionalities by endcapping each PU-2 chain with silane groups. APTS can also react with carboxylic acid groups along the PU-2 polymer chain, resulting in inorganic groups grafted as side groups along the polymer backbone. Water (pH = 5.0) at a molar ratio $[H_2O]/[TEOS]$ of 4:1 was added to a 50 wt. (%) solution of PU-2 modified with APTS in DMF. TEOS was then introduced into the solution in different quantities. Table 2 shows the amount of TEOS used to produce C2 samples and also the theoretical inorganic content incorporated into PU-2, assuming that all silane molecules were converted into siloxane bonds. Samples were cured as described for C1 samples. Curing of the two systems led to production of C1 and C2 samples in the form of disks (diameter 2-3 cm, thickness 0.1-0.2 cm). Figure 1 illustrates the chemical reactions processed during the production of C2 samples.

2.3. Characterization

Swelling measurements were used to estimate the degree of crosslinking of the polyurethanes[1] having progressively higher degrees of chemical modification through the introduction of inorganic species. Small pieces of cured sample were weighed (w_i) and extracted in DMF at room temperature for 24 hours. The specimens were then removed from DMF and placed in an oven at 60 °C for 18 hours. They were immersed again in DMF at room temperature for 24 hours (time required for swelling to reach equilibrium). After removing the specimens from DMF, the excess DMF solvent was removed with a dry cloth, and the specimens were weighed to determine the final weight (w_f). The percentage of increase in weight was calculated by using the relationship $(w_f – w_i) / (w_i) \times 100$.

Infrared spectroscopic experiments were carried out on a Perkin-Elmer Spectrum 1000 Fourier transform infrared spectrometer (FTIR).

Table 1. Inorganic content in PU-1 after reaction with hTEOS (C1) and theoretical values of SiO_2.

Samples	TEOS content (%)[a]	Theoretical SiO_2 content (%)[b]
C1-A	-	6.75[c]
C1-B	17.24	13.36
C1-C	29.41	18.93
C1-D	38.46	23.96
C1-E	51.02	32.37
C1-F	55.56	35.82

[a]wt. (%) of TEOS taking in account only TEOS and the polymer free of solvent; [b]Theoretical wt. (%) of SiO_2 calculated assuming that 221 g of APTS produces 60 g of SiO_2 and 208 g of TEOS produces 60 g of SiO_2; and [c]Theoretical wt. (%) of SiO_2 from APTS incorporated into PU-1 only.

Table 2. Inorganic content in PU-2 after reaction with TEOS (C2) and theoretical values of SiO_2.

Samples	TEOS content (%)[a]	Theoretical SiO_2 content (%)[b]
C2-A	-	10.19[c]
C2-B	18.18	15.08
C2-C	30.77	19.46
C2-D	40.00	23.41
C2-E	52.63	30.26
C2-F	57.14	37.94

[a]wt. (%) of TEOS taking in account only TEOS and the polymer free of solvent; [b]Theoretical wt. (%) of SiO_2 calculated assuming that 221 g of APTS produces 60 g of SiO_2 and 208 g of TEOS produces 60 g of SiO_2; and [c]Theoretical wt. (%) of SiO_2 from APTS incorporated into PU-2 only.

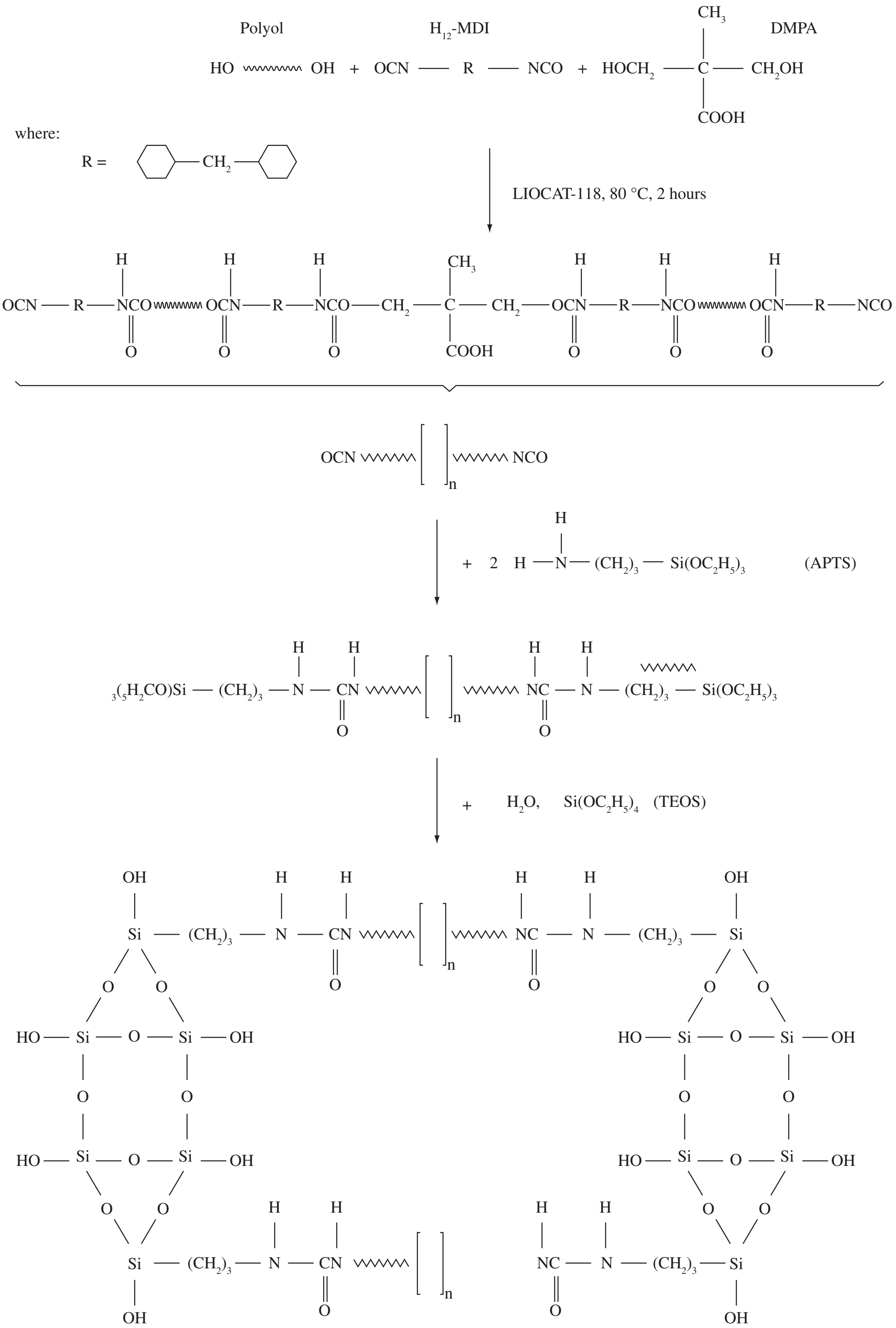

Figure 1. Chemical reactions involved in the production of C2 samples. Chemical reactions involved in C1 samples were the same except for the use of the DMPA reagent.

Typically, 32 scans at a resolution of 4 cm^{-1} were recorded of each sample by using an ATR (Attenuated Total Reflection) apparatus.

Thermogravimetric analyses (TGA) of samples were performed under N_2 atmosphere in a Shimatdzu TGA-50 equipment. Samples averaging 10 mg in weight were heated from ambient temperature to 900 °C at a heating rate of 20 °C/min. The residue/ash was considered as due to the inorganic content of the materials.

Differential Scanning Calorimetry (DSC) analyses were carried out under N_2 atmosphere in a Shimadzu DSC-50 equipment. The samples were initially scanned over the temperature range from ambient to 200 °C at a heating rate of 10 °C/min to eliminate any possible volatile residue. The samples were then cooled and scanned again from –100 to 200 °C with a heating rate of 10 °C/min. The reported results were taken from the second heating run.

3. Results and Discussion

The visual aspect of inorganic modified PU´s was found to be highly dependent on the type of polyurethane. Polyurethane containing carboxylic acid groups (PU-2), when modified with inorganic entities, led to the production of cured samples highly transparent and with a smooth surface, as shown in Figure 2. On the other hand, samples produced by attaching inorganic species to PU-1 (polyurethane with no carboxylic acid groups) were slightly cloudy and also presenting an irregular surface. This result suggests that the introduction of more polar groups (carboxylic acid groups) within the backbone of polyurethanes improved the compatibility between polymer and inorganic species, leading to the production of smaller siloxane rich domains that would then scatter less visible light. Transparency has been used in other works to indicate compatibility[17].

The results of the swelling experiments are shown in Figure 3, where the swelling ratio is plotted as a function of the inorganic content of the modified polyurethanes. In order to obtain the inorganic content of the cured samples (i.e. after hydrolysis and condensation of silanes), it was assumed that 75% of the alkoxy groups turned into Si-O-Si units according to other works[18]. Theoretical curves were constructed by applying the rule of mixture on the inorganic content and swelling ratio, assuming that the inorganic entities of the samples would not expressively swell in DMF (theoretical swelling = swelling ratio of the pure PU times the fraction of the polymer in the samples) and also that the inorganic entities would not change dramatically the degree of interaction between the basic PU and the solvent. The theoretical curves would then assign an ideal behavior in which part of the polymer is being replaced by other stable component. In Figure 3, it is possible to realize that swelling ratio was dramatically reduced when polyurethanes were activated to incorporate inorganic entities by reacting them with APTS. This remarkable reduction in swelling is due mainly to the formation of siloxane crosslinks between endcapped PU chains and indicates that alkoxy groups at the end of polymer chains were hydrolyzed and reacted to form inorganic cross-links during network formation. In PU-2, carboxylic acid groups along the polymer chains can also interact with APTS derived species to form hydrogen bonds. These interactions could then occur along the polymer chains in inorganic modified polyurethanes derived from PU-2, reducing further chain mobility. Inorganic entities also acted as rigid cross-links, reducing chain mobility and consequently the swelling ratio. When TEOS was used to incorporate higher inorganic contents into the polymers, the swelling ratio of both type of polyurethanes (PU-1 and PU-2) tended to decrease. The rates of reduction in swelling ratio (i.e. the slope of the curves) were very similar to the slope of the theoretical curves. This result suggests that the incorporation of new inorganic moieties (from TEOS) to APTS modified polymers occurred without the formation of extra cross-links. Therefore, it can be proposed that inorganic entities, incorporated from TEOS, combined with alkoxy groups from APTS to form thicker cross-link regions instead of creating new smaller inorganic domains that would restrict chain mobility and swelling. Figure 3 also shows that the swelling ratio of PU-2 (polyurethane containing carboxylic acid groups) was lower than PU-1. This result suggests that carboxylic acid groups can enhance the formation of hydrogen bonds between chains, thus reducing chain mobility and swelling.

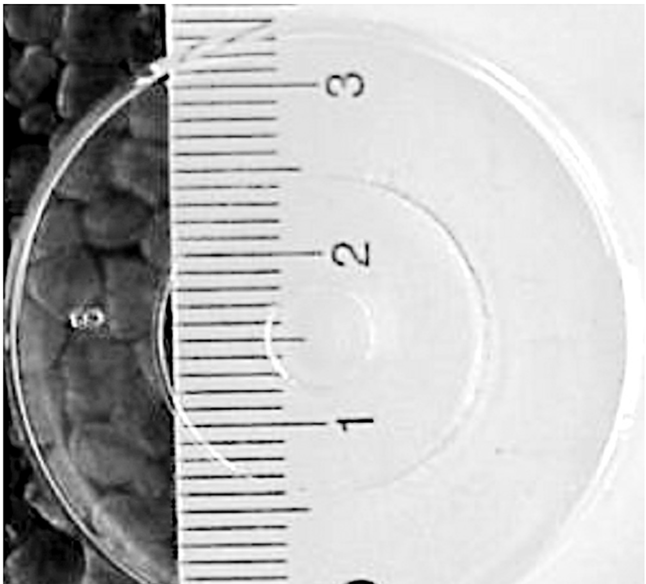

Figure 2. Photo of a C2-D sample.

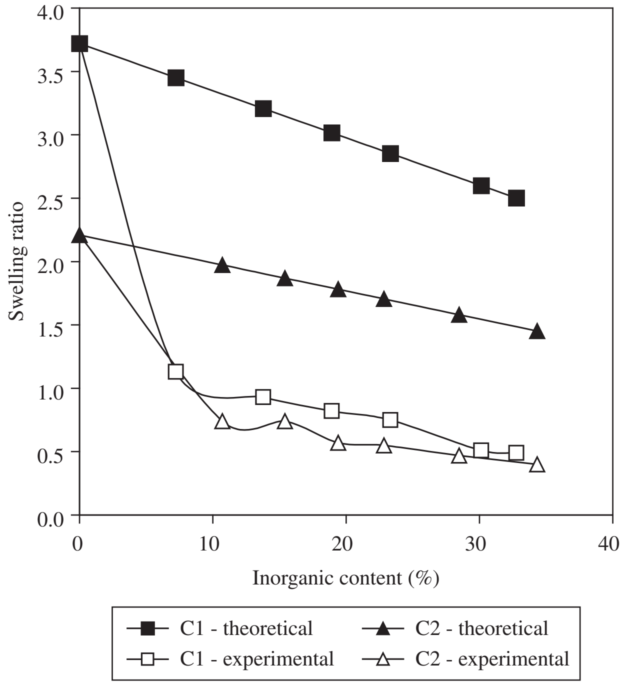

Figure 3. Effect of the incorporation of inorganic moieties on the swelling ratio of the modified polyurethanes.

FTIR spectra of the polyurethane with no carboxylic groups (PU-1) and the modified polyurethanes having inorganic entities (C1) are shown in Figure 4. Characteristic absorption bands related to polyurethanes can be observed in all four spectra in Figure 4, such as[19,20]: the 1715 cm^{-1} band, due to the carbonyl groups in urethane bonds (C=O); the 1550 cm^{-1} band, usually assigned to secondary amide (RCONHR'); the 1630 cm^{-1} band, assigned to carbonyl groups in urea bond; the 1150 cm^{-1} band due to C-O stretch; the 3400 cm^{-1} and 2900 cm^{-1} bands from N-H and C-H groups. According to Figure 4, the comparison between FTIR spectrum of PU-1 (Figure 4a) and the modified polyurethane having inorganic groups from APTS (C1-A) (Figure 4b) shows that the 1630 cm^{-1} band in Figure 4b, due to the carbonyl groups in urea bond, had a stronger absorbance than the 1715 cm^{-1} band while the reverse was observed for the PU-1 spectrum in Figure 4a. This result indicates that the amine group of the APTS had reacted with isocyanate groups at the polyurethane pre-polymer to form urea in a larger concentration than in the pure PU-1 polyurethane.

Absorption bands due to inorganic bonds, such as Si-O-Si and Si-OH, can be identified respectively at 1100-1040 cm^{-1} and 970-940 cm^{-1} in Figure 4. In the case of PU-1, the absorption band at 1100 cm^{-1} is also due to the ether C-O-C stretching. It is also possible to note that these bands due to the siloxane bonds became more intense and dominate the spectra as the inorganic content was increased, with the above-mentioned ether absorption band overlapping with the Si-O stretching vibration band. In order to emphasize the aspects of interest owing to the presence of inorganic moieties, a mathematical procedure involving subtracting the spectrum of the polymer (PU-1) from the spectrum of each inorganic modified polyurethane was performed to try to erase the overlapping between ether (due to PU) and siloxane absorption bands. Results are displayed in Figure 5 and are useful to illustratively reveal the presence and structural characteristics of the inorganic species. Analyzing the spectra, it was observed that characteristic absorption band due to Si-O-Si bonding (1040 cm^{-1}) became broader as the inorganic content in the polymer increased. This type of analysis suggests that the introduction of TEOS in the system led to progressively the incorporation of Si-O-Si bonds in the polymer and the formation of domains rich in inorganic species.

In Figure 6, FTIR spectra of the polyurethane containing carboxylic acid groups (PU-2, Figure 6a) and PU-2 modified with inorganic entities (C2) are shown. It is again clear the presence of IR absorption bands due to inorganic groups at 1100-1040 cm^{-1} and 970-940 cm^{-1} and carbonyl groups (1640 cm^{-1}) in urea due to the reaction between APTS and isocyanate at the end of polymer chains. Figure 7, the spectrum of pure PU-2 was subtracted from spectra of the inorganic modified polyurethanes shown in Figure 6. The results of this spectral subtraction reveal the presence of wide absorption bands at 1100-1040 cm^{-1} and 970-940 cm^{-1} due to inorganic domains located mainly at the crosslinking nodes of the polymeric network and in the free volume among chains.

The 1180 cm^{-1} band, observed in spectra in Figure 5 and 7, can be used to evaluate the degree of perfection of the formed inorganic Si-

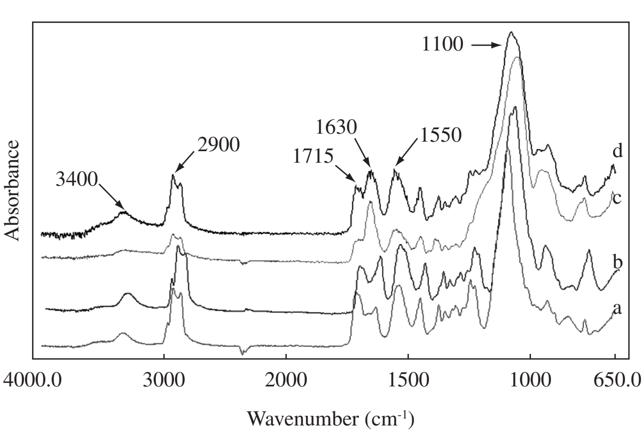

Figure 4. FTIR spectra of a) pure polyurethane PU-1 and polyurethanes having inorganic moieties: b) C1-A; c) C1-D; and d) C1-E.

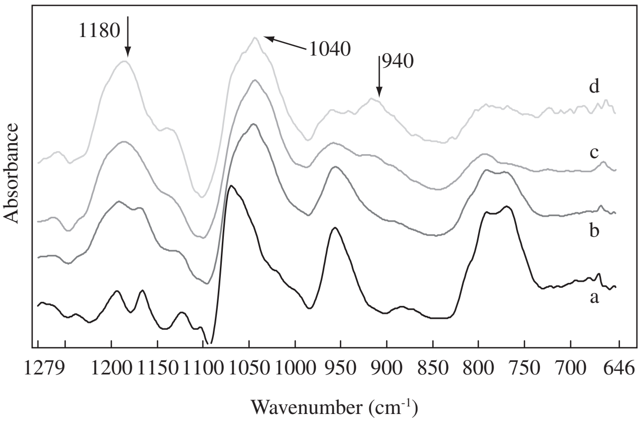

Figure 5. C1 FTIR spectra subtracted from the spectrum of PU-1: a) C1-A; b) C1-C; c) C1-D; and d) C1-F.

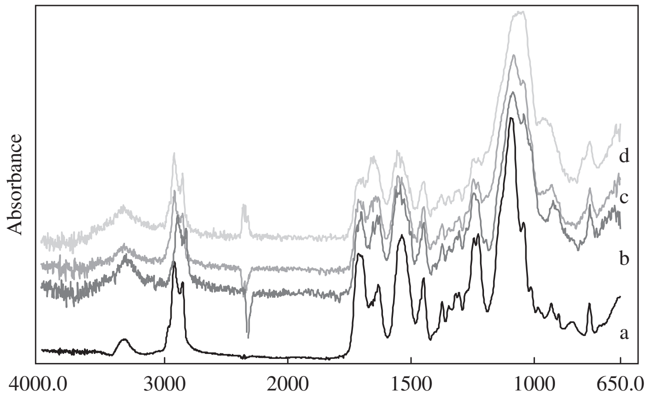

Figure 6. FTIR spectra of a) pure polyurethane containing carboxylic acid groups PU-2 and polyurethanes having inorganic moieties derived from PU-2: b) C2-A; c) C2-C; and d) C2-D.

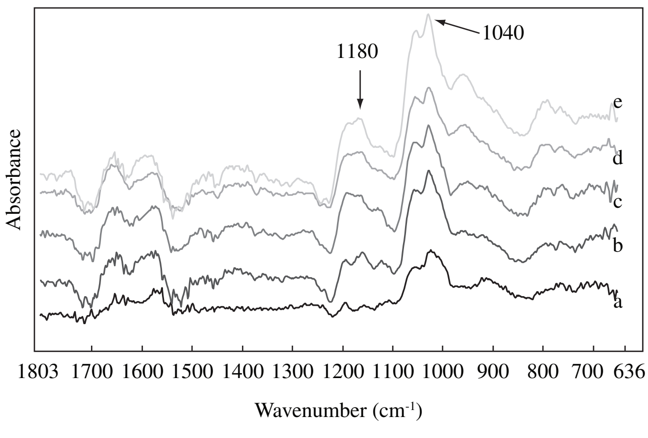

Figure 7. C2 FTIR spectra subtracted from the spectrum of PU-2: a) C2-A; b) C2-B; c) C2-C; d) C2-D; and e) C2-E.

O-Si domains[18], i.e. high density of cross-links and highly condensed network. The ratio between the absorbance of the 1040 cm^{-1} (Si-O-Si stretch vibration) and 1180 cm^{-1} in each spectrum can then be used to suggest structural differences among different types of modified polyurethanes regarding the formation of the inorganic domains. In Figure 8, it is shown that, at higher inorganic contents, the 1180 cm^{-1} band has a tendency to become more intense for both types of modified inorganic polyurethanes derived from PU-1 and PU-2. This fact suggests that the progressive incorporation of inorganic bonds in polyurethanes led to the formation of more perfect Si-O-Si domains that would contain higher density of inorganic cross-links and a lower concentration of unreacted alkoxy groups. This result is consistent with the swelling experiments which suggested that the insertion of new inorganic bonds, through the introduction of TEOS, within the modified polymer occurred rather by the growth of inorganic domains nucleated at the pre-existing inorganic functionalities on polyurethanes than by creating new small size domains throughout the material.

It is also evident in Figure 8 that the ratio between the 1040 cm^{-1} and 1180 cm^{-1} bands was higher for inorganic modified polyurethanes C2 (derived from PU-2, polyurethane with carboxylic acid groups) than for inorganic modified polyurethanes C1 (derived from PU-1, polyurethane with no carboxylic acid groups). This result can suggest that, in C1 materials, siloxane domains with lower amount of defects were formed, possibly due to the stabilization of a more intense phase separation process that would result in the aggregation of densely packed inorganic molecules in larger inorganic domains. On the other hand, carboxylic acid groups on polyurethanes were able to promote higher degrees of phase compatibility that resulted in inorganic domains with smaller sizes.

TGA curves of the pure PU-1 and inorganic modified polyurethanes derived from PU-1 (C1) are shown in Figure 9, while TGA curves of the C2 system are shown in Figure 10. The weight loss after heating the polymers up to 900 °C was used to estimate the inorganic content incorporated in the materials, even though the TGA analyses were performed in N_2 atmosphere instead of O_2, resulting possibly in a solid residue of the hybrid materials that may contain not only silica but also C. Nevertheless, the obtained values were considered a reasonable approximation of the inorganic content of the hybrid materials, since the calculations took into account that each hybrid material was derived from the same PU that left a very small residue after being heated up to 900 °C (less than 1%). Results showed that the inorganic content incorporated within the polyurethanes were close to the predicted values (theoretical values shown in Tables 1 and 2). No major change in the temperature of the thermal degradation was noted when inorganic entities were added to PU-1. However, a shift of the temperatures of thermal degradation to higher values was observed when inorganic moieties were incorporated in PU-2 (Figure 10). This result is an indication that the inorganic domains were more homogeneously distributed in the C2 material, being then able to more successfully protect the polymer backbone and delaying the onset of major chain scission. Insets in Figures 9 and 10 show the first derivatives (DTGA) of some TGA curves in order to emphasize the differences in thermal behavior when inorganic entities were inserted into PU-1 vs. PU-2.

The thermal properties of PU-1 and C1 modified polymers were further investigated by DSC, and results are shown in Figure 11. The measured T_g (glass transition temperature) of the soft segment of the

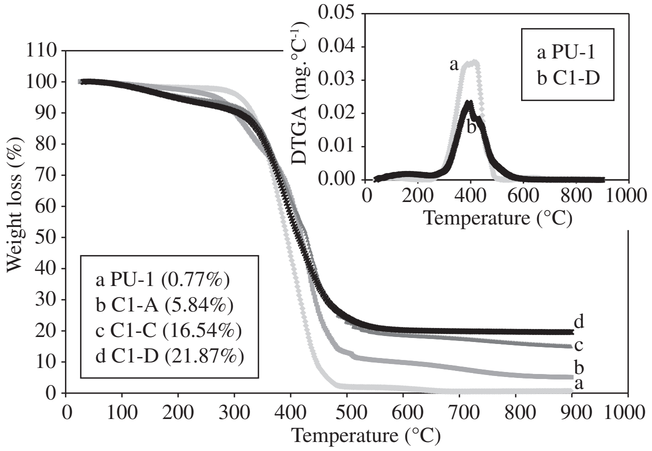

Figure 9. TGA curves of the PU-1 and inorganic modified polyurethanes derived from PU-1 (C1). In brackets: the experimental inorganic content (percent of the samples left after heating up to 900 °C). The inset shows the first derivative of TGA curves for samples PU-1 and C1-D.

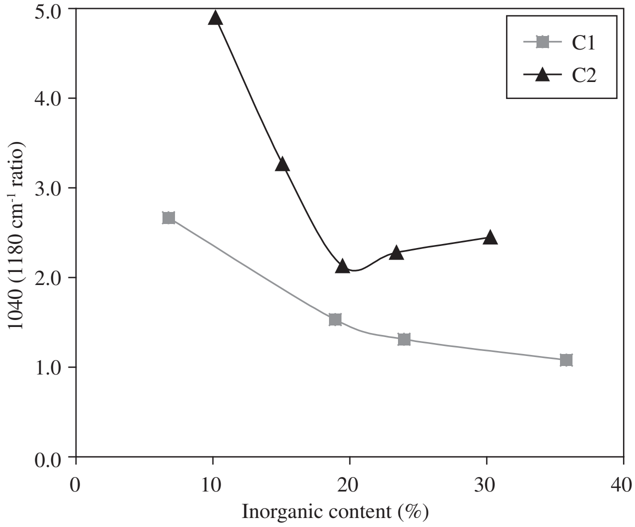

Figure 8. Dependence of the 1040/1180 cm^{-1} absorption band ratio on the inorganic content of C1 and C2 modified polyurethanes.

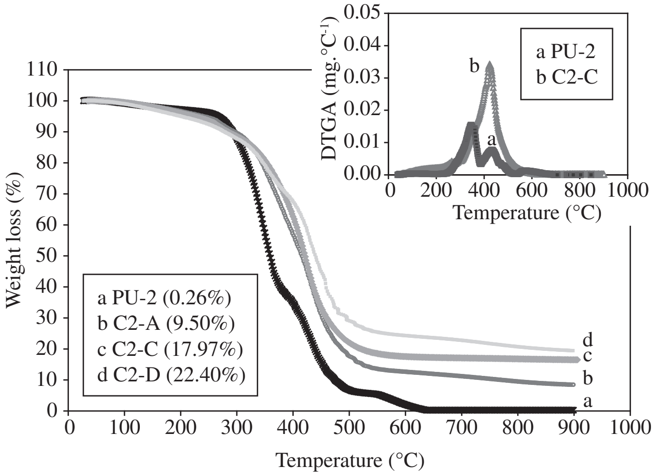

Figure 10. TGA curves of the PU-2 and inorganic modified polyurethanes derived from PU-2 (C2). In brackets: the experimental inorganic content (percent of the samples left after heating up to 900 °C). The inset shows the first derivative of TGA curves for samples PU-2 and C2-C.

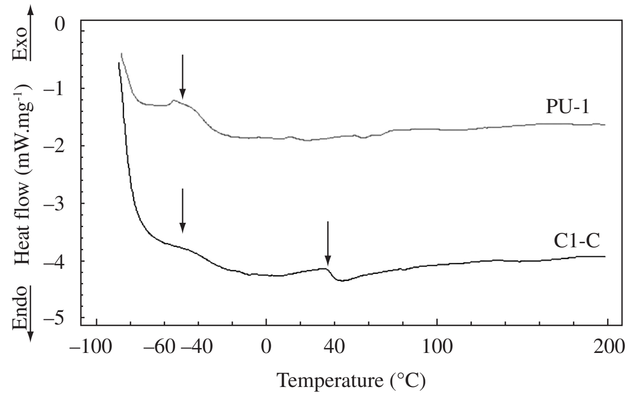

Figure 11. DSC curves of the PU-1 and inorganic modified PU-1 (C1-C).

neat PU was –35 °C. On the other hand C1-C sample (inorganic modified polyurethane derived from PU-1) presented two T_g's in DSC curve. The first one at the same range of net PU, and another at 40 °C probably due to the presence of inorganic groups that acts as cross-linkers and reduces the mobility of the polymeric chains. This result could be attributed to the morphology of relatively immiscible microphases. One of the microphases corresponding to Si-O rich domains and the other one based on net PU. The microphase-separated morphology is in accordance with the slightly cloudy visual aspect of C1 samples.

4. Conclusions

Aliphatic polyurethanes were successfully modified with inorganic entities to produce structurally and compositional different polymeric networks. Carboxylic groups along polyurethane chains were able to yield tough and transparent materials, while polyurethanes with no carboxylic acid groups led to the production of more translucent samples (that might suggest the presence of a less compatible system that would possibly phase separate in larger domains capable of scattering visible light). The inorganic content of the materials varied between ~7 and ~38 wt. (%) and the values obtained using TGA, despite the use of N_2 atmosphere, were very close to the predicted values. The temperature of the onset of thermal degradation was shifted to higher temperatures due to the presence of the inorganic moieties, particularly in polyurethanes having carboxylic acid groups (C2 system). The inorganic modified polyurethane derived from PU-1 showed two glass transition temperatures, probably due to phase-separated morphology. The results showed that the inorganic entities can reduce chain mobility and protect the polymer backbone to delay the onset of chain breakage. FTIR studies together with the swelling experiments suggested that more fully condensed and cross-linked inorganic entities were present in less polar polyurethanes (with no carboxylic acid groups), as an indication of a tendency towards a more phase-separated system. On the other hand, in more polar polyurethanes (polyurethanes containing carboxylic acid groups), the inorganic entities were proposed to be present in smaller domains, where the inorganic molecules were less packed and cross-linked. Results also suggested that the progressive incorporation of inorganic moieties in both types of polyurethanes occurred in regions previously activated with inorganic functionalities, instead of by the creation of new domains.

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