Effect of Silica Modification on the Chemical Interactions in NBR-Based Composites

Juan F. Lopez,[1] Leon D. Perez,[1,2] Betty L. Lopez[1]

[1]Materials Science Research Group, Institute of Chemistry, University of Antioquia, Medellín, Colombia
[2]Department of Materials Engineering, University of Antioquia, calle 62 No.52-59 SIU Lab 310 Medellin, Colombia

ABSTRACT: Fillers are modified with the purpose of increasing their interactions with polymer matrices; however it is necessary to determine the impact that those modifications have on the composite performance and morphology. In this work, the strength of the chemical interactions between silica with different chemical characteristics and acrylonitrile butadiene rubber (NBR) is studied by infrared spectroscopy measuring the increase of $C \equiv N$ fundamental vibration frequency and by density functional theory (DFT) and *ab initio* methods. The results from the chemical interactions were compared with the morphology and thermal behavior of composites based on those components. Good agreement between the molecular parameters estimated theoretically and the shifting of the absorption frequency due to $C \equiv N$ stretching was observed. Morphological studies revealed that the steric hindrance exerted by modifier moieties on silica surface favors the filler dispersion. Functional groups on the surface strongly interacting with NBR play an important role in the compatibility of immiscible blends of NBR copolymers studied in this work. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2130–2138, 2011

Key words: silica; surface modification; polymer nanocomposites; chemical interactions

INTRODUCTION

High performance materials based on polymers are obtained by the use of fillers which endow them the desired mechanical, thermal, and electrical properties.[1,2] The degree of improvement of those properties is strongly dependent on filler concentration and characteristics, such as particle size, specific surface area, shape, dispersability, and chemical affinity with the polymer matrix.[3–7]

The morphology of polymer composites depends on three competitive phenomena[8]; filler aggregation, formation of supramolecular polymer structures, and anchoring of polymer chains at the filler surface. In the case of silica, attaining good dispersion of the particles is challenging since they are polar solids and tend to form aggregates instead of interacting with slightly polar polymer matrices. However, silica fillers are widely used in the reinforcement of elastomers[9–12]; due to their low cost, less prejudicial impact on the environment[13] and the ability to confer lower rolling resistance and higher wet grip strength to the filled elastomers, which is particu-larly important in technological applications such as tire fabrication.

Favorable filler and polymer chemical interactions allow obtaining good reinforcement; since the dispersion of the filler and the formation of an adsorbed polymer layer around the filler particles are facilitated.[14–16] The most feasible way to enhance the strength of the interactions is the modification of the filler surface. Nevertheless, dispersion of the filler can also be enhanced by either reducing the polarity of the filler particles or sterically avoiding their aggregation.[17,18] In the case of silica, the surface modification is favored by the presence of highly reactive isolated silanol groups.[19,20] For example, silane coupling agents containing sulfur are widely used in the tire industry to increase the dispersability of silica into elastomeric matrices and promoting the formation of covalent bonds between the phases.[21–23]

Computational modeling using DFT and *ab initio* methods can be a useful tool to estimate the effect that a particular chemical moiety on the filler surface has on the strength of chemical interactions with an elastomeric matrix. A reasonable approach is to rank the interaction energy of one particular elastomer and a set of possible modifications by using theoretical models. The determination of this information by experimental methods is more complex, since some properties such as morphology depend on the sample preparation, and expensive because a single characterization technique does not provide enough evidence.[24,25]

This article is focused on studying the effect that the modification of silica with different types of functional groups has on the morphology and thermal behavior of composites based on NBR. The silica was modified with electron donor, alkaline, and acid groups; the strength of the interaction NBR–filler was studied by theoretical calculations and by infrared spectroscopy and those results were compared to the composite morphologies and thermal properties.

EXPERIMENTAL

Materials

Fumed silica, with an average particle size around 7 nm and surface area of 390 ± 40 m^2 g^{-1}, silane reagents: triethoxyvinylsilane 97% (TEVS), (3-Aminopropyl) trimethoxysilane 97% (APTMS) and (3-Mercaptopropyl) trimethoxysilane 95% (MPTMS), benzoyl peroxide, and tetrahydrofuran chromatographic grade (THF) were purchased from Sigma-Aldrich and NBR with 33 wt % Acrylonitrile ($M_w = 2.5 \times 10^5$ Da, PD = 3.5) from Bayer.

Samples preparation

Silylation of silica

Prior to the functionalization reaction, fumed silica was dried at 200°C for 24 h under vacuum to eliminate the weak bounded water and other species adsorbed on its surface, then, the powder was dispersed in THF using an ultrasound bath for 10 min. The silylation reaction was carried out under nitrogen atmosphere at 60°C for 24 h and the amount of silane required for the reaction was calculated assuming a 1 : 1 molar ratio and considering the larger possible concentration of silanol groups on this kind of material which according to Dugas and Chevalier is around 8 μmol m^{-2}.[26] To modify the silica surface with sulfonic acid groups, the solid previously modified with MPTMS was treated with 5 v/v% hydrogen peroxide at room temperature for 24 h to oxidize the thiol group (—SH) and produce —SO$_3$H.

Composites preparation

The composites were prepared as follows; first, the corresponding amount of silica was thoroughly dispersed in THF in an ultrasound bath, then proper amounts of NBR (5 wt % respect to THF) were added to the filler dispersion. The resulting slurry was heated at 37°C and magnetically stirred until obtaining a homogeneous dispersion and kept at room temperature for 24 h. Finally, benzoyl peroxide (3 wt % respect to the rubber) was added to the dispersion, the resulting blend was maintained in an open vessel with stirring until the solvent was completely elimi-

nated. The samples thus obtained were treated at 100°C and 21 MPa to promote the crosslinking.

Abbreviations for samples name contain N to indicate that the matrix is NBR followed by a number indicating the amount (wt %) of filler. In the case of modified silicas, A, V, or S before concentration indicates that the functional group used to modify the filler was amino, vinyl or sulfonic acid, respectively.

Silica characterization

Infrared study of silylated silica samples

The modification with different alkoxysilanes was evaluated by Fourier Transform Infrared Spectroscopy (FTIR) in a Spectrum One spectrometer supplied by Perkin–Elmer, USA. The spectra showed that, in addition to typical infrared bands for silica, the silylated materials exhibited distinctive bands due to the organic groups on modifier. For instance, bands at 2930 and 2870 cm^{-1} and at 1455 cm^{-1} due to the stretching and bending deformation of C—H and the presence of bands at 3300 and 1655 cm^{-1} corresponding to —NH$_2$ stretching and scissoring, confirms that the modification with APTMS was successful.

In the case of vinyl functionalized silica two absorption bands were detected; one due to olefinic C—H stretching at 3057 cm^{-1} and C=C stretching vibration at 1602 cm^{-1}. The modification with sulfonic acid was verified by the presence of absorption bands at 2950, 2890, and 1347 cm^{-1} due to the alkyl and —SO$_3$H groups, respectively.

Composites characterization

Infrared study of silica samples impregnated with NBR

Silica samples were impregnated with NBR as follows: a THF dispersion of silica (5 wt %) and polymer (1 wt %) was kept under stirring at room temperature during 24 h and then centrifuged. The remaining solid was dried under reduced pressure during 2 days and then dispersed in KBr for the analysis. To reduce the amount of silanol groups on the silica surface, for this characterization, the grafted silica samples were synthesized by direct condensation of the respective silane reagents in an acid aqueous medium at room temperature, the reaction was maintained under stirring until a white slurry was observed, then the solid was separated by centrifugation and carefully dried at 80°C.

Scanning electron microscopy analysis

Morphology of the solvent-casted composite films was studied by scanning electron microscopy (SEM).

A

Modifications

B

Probe Molecules

Elastomer

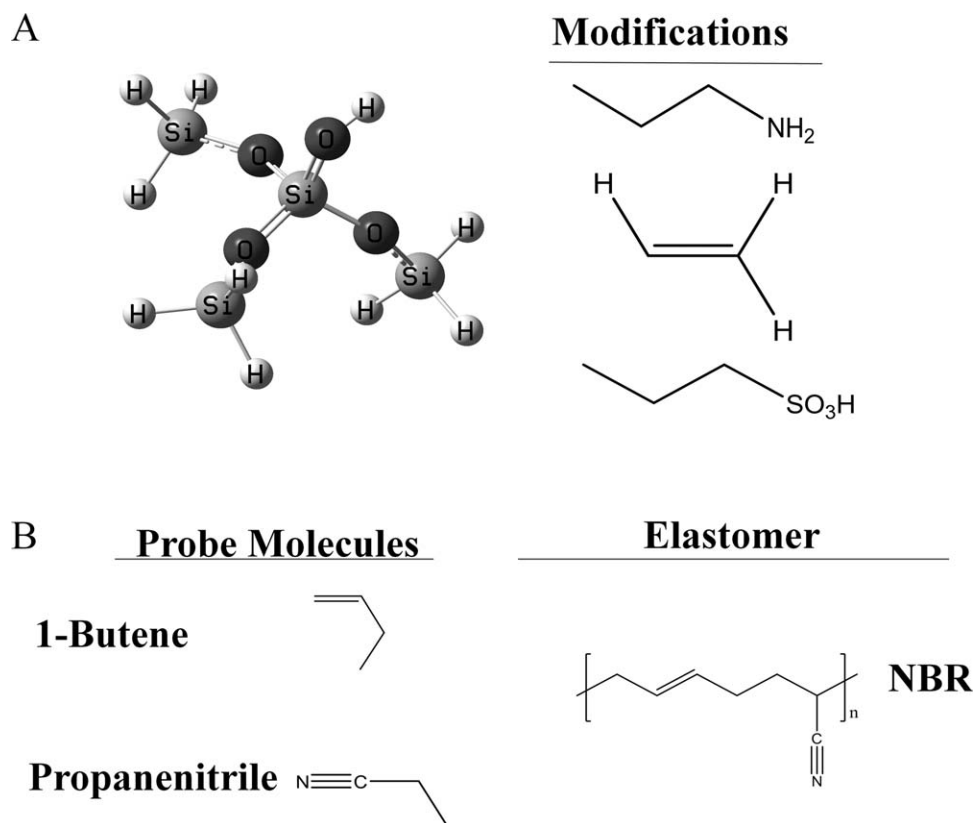**1-Butene**

NBR

Propanenitrile

Figure 1 Molecular structures used in the calculations. A. structures analogous to the local chemical environment of the silica surface with the corresponding modifications. B. Elastomer structure and their corresponding analogous probe molecules.

A droplet of a diluted dispersion of polymer and the respective filler in THF was deposited on an aluminum sample holder and kept at room temperature until the solvent was evaporated to form a thin film. A JEOL JSM-6490LV scanning electron microscope equipment was used for the characterization.

Thermal analysis

Glass transition temperatures (T_g) were measured by modulated differential scanning calorimetry (MDSC) in a Q100 calorimeter supplied by TA Instruments, USA. The samples were heated from 20 to 150°C at 20°C min^{-1} and isothermally maintained for 5 min, then cooled to -90°C at 20°C min^{-1}. The thermograms were collected from -90 to 10°C, the total heating rate was 3°C min^{-1} and modulated at 1°C every 60 s.

COMPUTATIONAL DETAILS

Figure 1 shows the structure of the molecules used to represent the local chemical environment of the silica surface with the corresponding modifications also studied experimentally, as previously described. In the models construction, a single isolated func-

tional group was considered. For instance, the unmodified silica besides isolated silanol groups also contains geminal and vicinal silanols, including them would make more complex the calculations since they interact through the formation of hydrogen bonds.

In spite of the fact that Si—H groups are not observed on the silica surface, at least if a reduction procedure is performed, Si—H bonds were included as terminal groups due to its lower polarity and reactivity compared to the silanol groups, for instance, the pKa value for —Si—OH and for SiH$_4$ are 7.0 and 35, respectively.

Calculations were performed as previously reported by Perez et al.[27] Full optimization of surface models, probes and complexes (surface + probe molecule) were carried out at the DFT level using the Becke three-parameter hybrid functional combined with Lee-Yang-Parr correlation functional (B3LYP). In particular, for the complexes, the functional group on silica and the probe molecule were relaxed. To have a better treatment of the electron correlation of the stationary points located with B3LYP, sophisticated second-order Møller-Plesset Theory (MP2) with a 6-311g(d) basis set energy calculations were carried out. This theory level offers
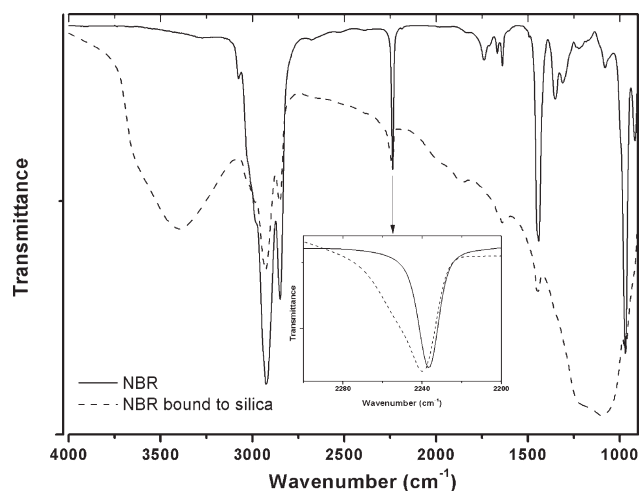
Figure 2 Infrared spectra of NBR impregnated to silica and the reference elastomer (the inset zooms the band due to stretching of the nitrile group on both samples).

higher sensitivity to weak interactions such as Van der Waals forces compared to B3LYP. Although the theoretical interaction energy calculated can deviate from the experimental values due to the inaccurate consideration of the electronic properties, for the purpose of this article only the interaction tendency is considered. The interaction energy (IE) was calculated according to eq. (1); the value is corrected by considering the basis set superposition error (BSSE):

$$IE = -[(E_{complex} - (E_{probe} + E_{surface})) + BSSE] \quad (1)$$

In the equation, $E_{complex}$ is the energy of the surface + probe molecule complex and E_{probe} and $E_{surface}$ are the energy of the probe molecule and the surface model at MP2/6-311g(d) theory level, respectively. For energetic properties, the BSSE corrections were done by using the full counterpoise method of Boys and Bernardi.[28] The charges were obtained by natural bond orbital analysis at MP2 theory level. All electronic structure calculations were carried out using the Gaussian 03 program.[29]

RESULTS AND DISCUSSIONS

Polymer and filler chemical interactions

From the thermodynamic point of view; the adsorption of macromolecules on solid surfaces can be described in terms of Gibbs free energy change which is a result of entropic and enthalpic contributions.[18] Entropy opposes to the adsorption, since when macromolecules are attached to a solid their conformational freedom is restricted.[30] Enthalpy is then the driving force and rises from the establishment of either strong covalent bonds or weak interactions such as hydrogen bonds, electron donor–acceptor interactions and dispersive forces. For that

reason, studying the strength of the polymer–filler chemical interactions allows favorable reinforcement to be monitored.

According to the infrared spectra shown in Figure 2, the vibration frequency of the symmetric stretching of the C≡N bond at 2237 cm⁻¹ in NBR impregnated to silica is significantly broadened and shifted to higher frequency (∼ 3.6 cm⁻¹) compared to the reference elastomer (see inset in Fig. 2), indicating the establishment of chemical interactions. It was demonstrated by Purcell and Drago that when acetonitrile forms a coordination complex with an electron donor molecule, the frequency of C≡N fundamental stretching vibration always increases. The increase in the vibration frequency is due to changes on coordination in the nitrogen 2s lone pair orbital which causes strengthening of the C≡N bond.[31]

To study the effect that the filler surface characteristics has on the strength of chemical interactions of silica with NBR; silica samples grafted with three different kinds of functional group; amino, sulfonic acid and vinyl were also impregnated with NBR and studied by FTIR. The results in Figure 3 and Table I show that the increase in the vibration frequency of the C≡N stretching depends on the modifier characteristics. For instance, surfaces containing silanol and sulfonic acid groups exhibit larger frequency shifts compared to vinyl and amine modified materials.

Computational results

According to the results previously mentioned and data reported by Costa et al.,[32,33] the interaction between NBR and silica takes place through the polar groups on both components. Estimation of the interaction energy of small molecules structurally
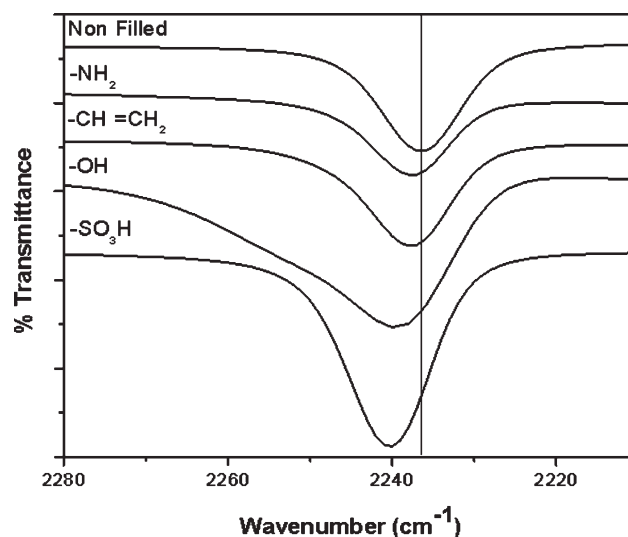

Figure 3 Magnification of the band due to —C≡N stretching for NBR bound to silica with different chemical moieties.

TABLE I
Molecular Parameters for the Complexes Propanenitrile + Surface Models and the
Infrared Shifts Determined Experimentally for $-C \equiv N$ Absorption Band of the NBR
Bound to Silica with Different Modifications

Surface group	IE (Kcal mol^{-1})	Surface–probe distance	Analysis of the natural charge transference		Infrared shifting (cm^{-1})
			Δq probe	Δq silica	
$-SO_3H$	9.34	1.82[a]	−0.11(N) 0.10 (C$_1$)	0.043 (H) −0.034 (O$_1$)[b] −0.022 (O$_2$) −0.013 (O$_3$) 0.023 (S)	3.8
$-OH$	6.61	1.95[a]	−0.080(N) 0.070(C$_1$)	−0.031 (O) 0.043 (H)	3.5
$-NH_2$	3.65	2.54 N⋯H$_1$ 2.96 H$_1$⋯N	−0.030 (N) 0.018 (C$_1$) −0.019 (C$_2$) 0.039 (H$_1$)	−0.027 (N) 0.019 (H$_1$) 0.005 (H$_2$)	1.1
$-CH=CH_2$	0.90	2.74 H$_1$⋯N	−0.018 (N) 0.016 (C$_1$)	0.006 (C$_1$) −0.019 (C$_2$) 0.02 (H$_1$) −0.006 (H$_2$) 0.001 (H$_3$)	1.6

[a] The distance listed corresponds to the separation between the N atom on the probe and the H on the surface model in the other cases.
[b] The atom labels correspond to those assigned in Figure 4.

analogous to the elastomer and a silica model is a proper approach for studying the strength of the chemical interactions between a polymer and a silica surface or at least could be helpful to determine the impact that a specific modification has on them. It was shown by Perez et al. that the interaction between silica and elastomers such as NBR, SBR and BR is strongly dependent on the functional groups on the elastomer i.e., nitrile, phenyl or alkene groups, respectively. The interaction order of the elastomers and silica agrees well with the order estimated theoretically using small molecules chemically similar to the elastomer and a silica model composed of a single isolated silanol.[27]

Acrylonitrile butadiene rubber is composed by both alkene and nitrile functional groups, as schematically shown in Figure 1. The chemical interaction between NBR and silica with different modifications was simulated by the interaction of 1-butene and propanenitrile probe molecules with a silica model grafted with the functional groups previously mentioned and shown in Figure 1. According to the interaction energy values listed in Table II, the nitrile compound interacts stronger with all the silica models than 1- butene. Additionally, a good correlation between the interaction energy and the acidity (see pKa range in Table II) of the functional group on silica was also found, except for the case of propanenitrile and amino grafted silica that will be considered later. In general, larger interaction energy values have been estimated when the surface model

contains sulfonic acid and silanol groups, for both probe molecules, compared to those estimated for vinyl and amine modified silica models.

Based on the computational and infrared spectroscopy results, the chemical interaction between NBR and silica is greatly favored by the presence of nitrile groups in the polymer chain. Molecular parameters for the complexes involving propanenitrile; such as interaction energy, natural charge transference on the complex formation as well as the distance between the molecules, determined theoretically for the structures showed in the Figure 4, are compared to the increase of the frequency for the symmetric stretching of the nitrile group on NBR impregnated to silica which are presented in Table I. It is clearly seen that the estimated interaction energy is related to the increase of the vibration frequency. Although, the

TABLE II
Interaction for Probe Molecules and the Surface Models
Estimated at MP2/6-311g(d)

	Interaction energy (kcal mol^{-1})			
Probes	$-NH_2$ (~ 44[a])	$-CH=CH_2$ (~ 40[a])	$-SO_3H$ (~ 0–1[a])	$-OH$ (7.2[b])
Propanenitrile	3.7	0.9	9.3	6.6
1-Butene	0.3	0.1	5.2	2.6

[a] Typical pKa values for the functional group in organic compounds.
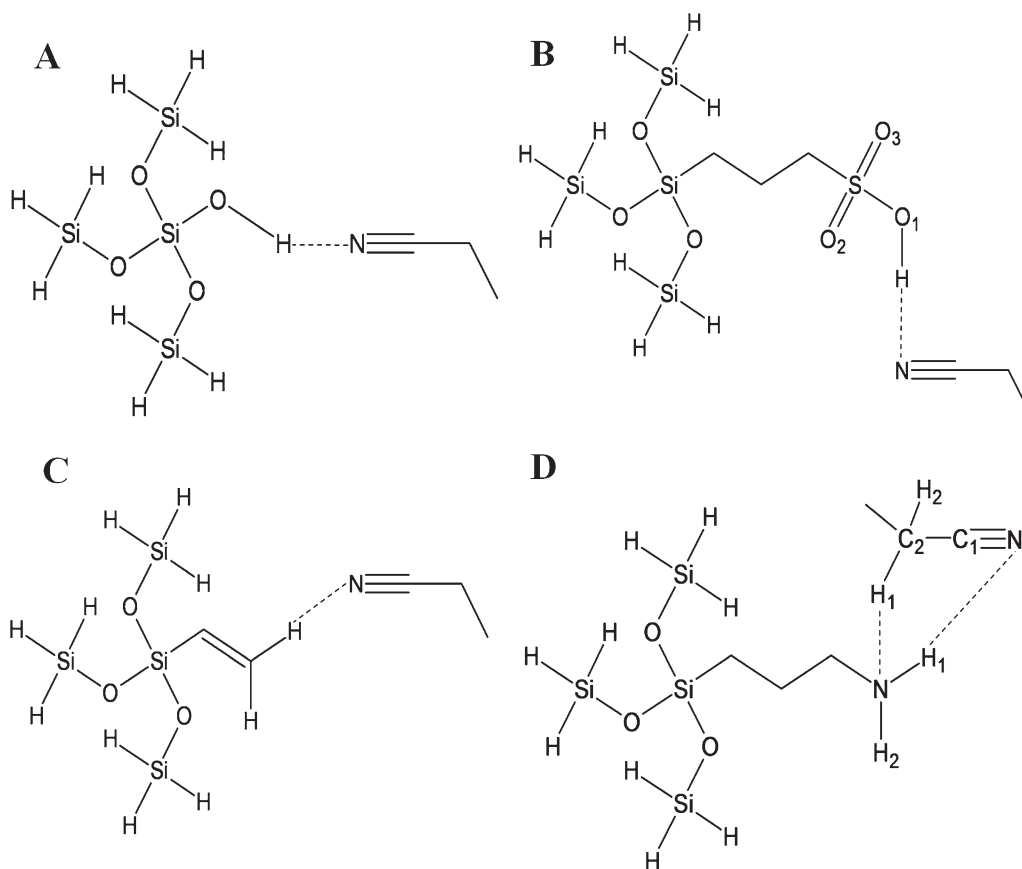[b] pKa value for silica according to Nawrocki[19].

Figure 4 Schematic representations of the equilibrium geometries for the complexes propanenitrile + surface models containing A. silanol, B. sulfonic acid, C. vinyl and D. amine units estimated at B3LYP/6-311g(d) theory level.

largest values were obtained in the cases of raw silica and silica modified with sulfonic acid groups and also corresponded to the most pronounced shift of the vibration frequency; in the case of silica grafted with amine groups, which presents a larger interaction energy than silica modified with vinyl units, the NBR impregnated to that material presented a lower increase in the vibration frequency of the $-C\equiv N$ bond.

As shown in Figure 4, the formation of the complex propanenitrile + $-NH_2$ grafted silica is due to two different weak hydrogen bonds,[34] they are, $H_{1surface}-N_{probe}$ and $H_{1probe}-N_{surface}$. According to the natural charge transference, and the distance between the atoms implicated in each bond, the interaction $H_{1probe}-N_{surface}$ is stronger than the interaction that involves the $-C\equiv N$ group.[35,36] It could explain the fact that although a stronger interaction energy is predicted for this complex a slighter increase in the vibration frequency of the $-C\equiv N$ is observed when compared to the same probe molecule interacting with vinyl modified silica. In this case a single interaction involving the nitrile group is predicted, which in turn, according to data in Table I, exhibits a shorter distance H—N in the surface and probe, respectively.

For the other complexes, the estimated distance between the interacting atoms and the charge transference let predicting the formation of moderated hydrogen bonds[34] and the interaction is basically of the type electron donor acceptor; being the $-C\equiv N$ the electron acceptor and silica the electron donor. The results show a good correlation between the theoretical interaction energy and the natural charge transference on the complex formation with the increase in the vibration frequency of the $C\equiv N$ bond measured by infrared spectroscopy.

Morphological study by SEM

SEM pictures of the solvent-casted composite films are presented in Figure 5. According to them, the modification with amine and vinyl groups [Fig. 5(B,C)] imparts better dispersion to the silica particles (smaller size of the aggregates) respect to the composite containing unmodified silica. Although, according to the previous results it is concluded that those groups interact weakly with polar groups on the polymer, the better dispersion can be due to the steric hindrance effect caused by the modifier which prevents silica particles from aggregating.
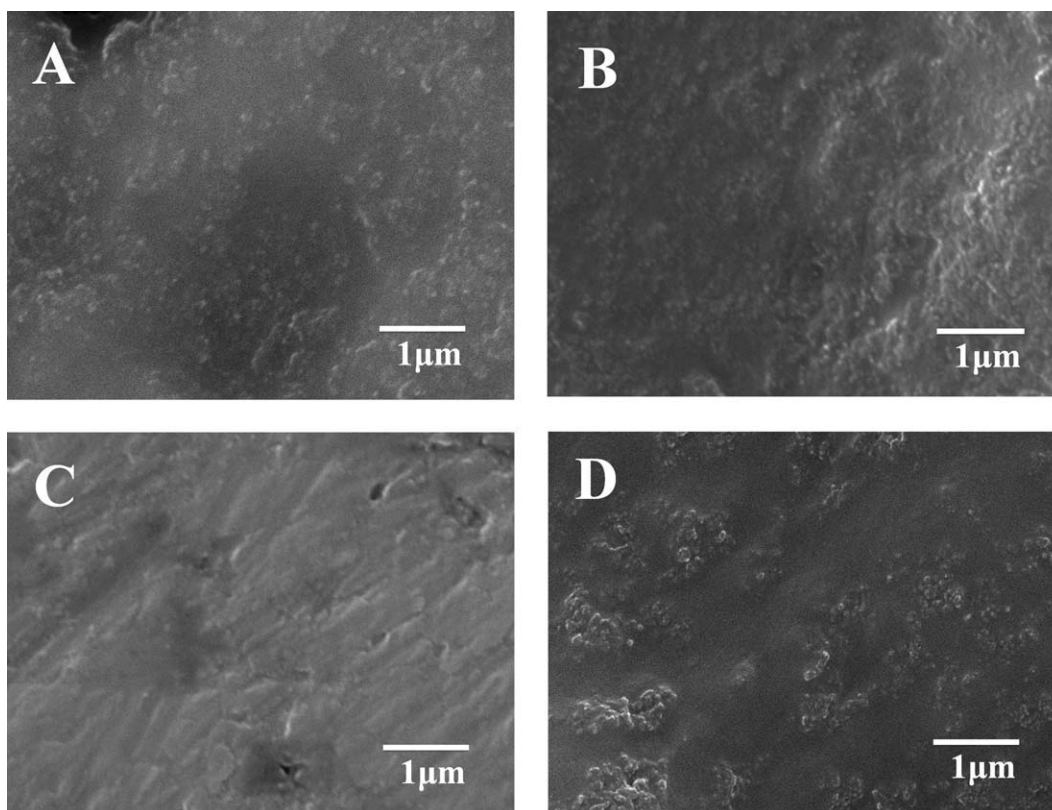
Figure 5 SEM pictures for the solvent - casted composites. A. N5, B. NV5, C. NA5, and D. NS5.

In the case of the composite NS5, Figure 5(D), the silica particles are forming large aggregates. Although —SO₃H group interacts strongly with the nitrile groups on the NBR, the aggregation of silica is due to the formation of interparticle hydrogen bonds which involve sulfonic acid groups as well as residual silanols.[37]

Thermal analysis

The impact of the chemical interactions between silica and NBR on the composites thermal behavior was evaluated by MDSC. Figure 6(A) presents the reversible thermogram for NBR and its composites filled with 5 wt % of silica with different surface characteristics, the T_g values are summarized in
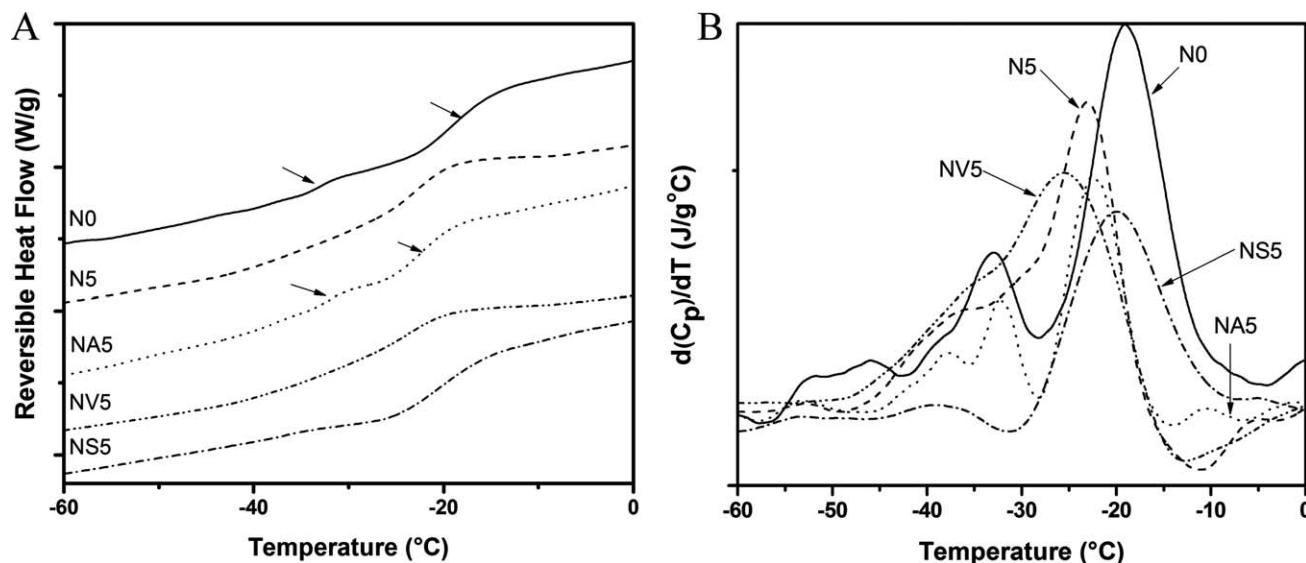

Figure 6 MTDSC plots for NBR and silica with different chemical modifications, A. reversible heat flow versus temperature. B. dC_p/dT versus T.

TABLE III
Glass Transition Temperatures for the Composites

Sample	T_g (°C)
N0	$-32.6 (T_{g1})$
	$-19.6 (T_{g2})$
N5	-23.9
NA5	$-31.9 (T_{g1})$
	$-22.2 (T_{g2})$
NV5	-22.0
NS5	-20.5

Table III. N0 exhibits two vitreous transitions; in concordance with Ambler[38] this thermal response is due to the presence of two immiscible copolymers with different compositions, which is observed when NBR is synthesized by emulsion polymerization at low acrylonitrile contents. The composite N5, NS5, and NV5 exhibit a single glass transition which takes place at an intermediate value between the two transitions observed for N0; this behavior indicates that the silica acts as a compatibilizer for the immiscible blend of copolymers.

It has been established that when a filler interact with both components in a binary immiscible blend improves the compatibility.[39,40] Reduction of the segmental mobility as well as the establishment of a complex interphase around the filler particles have been claimed to be responsible for that phenomenon.[18,41] Additionally, the plots dC_p/dT versus T in Figure 6(B) show that the single glass transition exhibited by the composite N5, NS5, and NV5 takes place in a broader range compared to N0 which is associated to the formation of a diffuse interphase supported by the presence of the filler.[39,40]

In the case of composites that exhibited a single T_g, the lowest value is observed for N5 while the highest values correspond to NV5 and NS5 (data in Table III). Although the particles of raw silica present strong chemical interaction with the polymer segments, they also tend to be aggregated which reduces the filler effective surface area. In the case of NV5 composite, the interaction between silica modified with vinyl groups and NBR is less favorable compared to the raw silica; the establishment of the interphase polymer-filler that conducted to the compatibilization of the blend of NBR copolymers can be attributed to two facts; first, the vinyl groups are small and therefore $-C\equiv N$ groups in the polymer can interact with residual silanol groups on the silica surface. Second, the crosslinking reaction also involves the vinyl groups on silica and thus the formation of the interphase polymer–silica is greatly favored as well as the filler particles dispersion, as deducted from SEM analysis.

For the composite containing silica modified with $-SO_3H$, the glass transition appears at higher tem-

peratures than the transition of the corresponding composite containing raw silica. This behavior can be attributed, first, to the strong interaction between sulfonic acid groups on the silica and nitrile groups on polymer which led improved compatibility, as discussed above. Second, the filler particles have a great tendency to aggregate, as supported by the morphological analysis; therefore, the trapping of polymer chains into interstitial macropores also contributes to reduce the bulk mobility.

A different behavior is observed for the composite NA5 which presents two glass transitions temperatures as found for unfilled NBR [data in Table III and Fig. 6(A)]. The modification with APTMS inhibits the filler to act as a compatibilizer; it indicates that the interphase around the silica particles was not established which is in good agreement with the results previously discussed. That modification does not enhance the strength of the chemical interactions with the polymer, additionally; the steric hindrance exerted by those groups avoids the particles to aggregate and the polymer chains to access to residual silanol groups on the silica surface.

CONCLUSIONS

The stretching vibration of the nitrile bond in the NBR is shifted to higher frequencies as the acidity of the functional group on the silica surface increases. A good correlation between the infrared shifting and the interaction order estimated by using computational modelation was found. It was found that the interaction between the NBR and silica fillers involves acid–base interactions. According to the computational and infrared spectroscopy results, the interaction order was $-SO_3H > -OH > -NH_2 > -CH=CH_2$.

The dispersion of the silica particles in NBR is influenced by the strength of the interactions polymer–filler and the nature of the surface modifiers. The dispersion of silica particles is improved if the modifier prevents the particles aggregation by steric hindrance.

High interaction polymer–filler increases the compatibility of the copolymers in the NBR matrix. A single T_g was detected when silica contained polar groups and vinyl units which react with the rubber chains during the crosslinking. No changes in the blend compatibility were observed for the modification with APTMS.

References

1. Mark, J. E. Acc Chem Res 2006, 39, 881.
2. Pavlidou, S.; Papaspyrides, C. D. Prog Polym Sci 2008, 33, 1119.
3. Bokobza, L. Polymer 2007, 48, 4907.

4. Morton, M.; Murphy, J.; Cheng, C. Copolymers, Polymer Blends, and Composites; American Chemical Society: Washington, DC, 1975; p 409.

5. Pérez, L. D.; López, J. F.; Orozco, V. H.; Kyu, T.; López, B. L. J Appl Polym Sci 2009, 111, 2229.

6. Perez, L. D.; Giraldo, L. F.; Brostow, W.; Lopez, B. e-polymer 2007, 029.

7. Heinrich, G.; Klüppel, M. Filled Elastomers Drug Delivery Systems; Springer: Berlin, 2002; p 1.

8. Peng, C. C.; Gopfert, A.; Drechsler, M.; Abetz, V. Polym Adv Technol 2005, 16, 770.

9. Lopez, B.; Perez, L.; Mesa, M.; Sierra, L.; Devaux, E.; Camargo, M.; Campagne, C.; Giraud, G. Annu Technical Conference—ANTEC, Conference Proceedings 2005; p 192.

10. Lopez, B. L.; Perez, L. D.; Mesa, M.; Sierra, L.; Devaux, E.; Camargo, M.; Campagne, C.; Giraud, S. e-polymer 2005, 018.

11. Perez, L. D.; Giraldo, L. F.; Lopez, B. L.; Hess, M. Macromol Symp 2006, 245/246, 628.

12. Brinke, J. W.; Debnath, S. C.; Reuvekamp, L. A. E. M.; Noordermeer, J. W. M. Compos Sci Technol 2003, 63, 1165.

13. Highwood, E. J.; Kinnersley, R. P. Environ Int 2006, 32, 560.

14. Vidal, A.; Haidar, B. Soft Mater 2007, 5, 155.

15. Gao, S.; Wang, Y.; Diao, X. Luo, G.; Dai, Y. Bioresource Technol 2010, 101, 3830.

16. Arroyo, M.; López-Manchado, M. A.; Valentín, J. L.; Carretero, J. Compos Sci Technol 2007, 67, 1330.

17. Aso, O.; Eguiazábal, J.; Nazábal, J. Compos Sci Technol 2007, 67, 2854.

18. Lipatov, Y. S. Polym Reinforcement; ChemTec Publishing: Canada, 1995.

19. Zhuravlev, L. T. Colloids Surf A Physicochem Eng Aspects 2000, 173, 1.

20. Nawrocki, J. J Chromatogr A 1997, 779, 29.

21. Castellano, M.; Conzatti, L.; Costa, G.; Falqui, L.; Turturro, A.; Valenti, B.; Negroni, F. Polymer 2005, 46, 695.

22. Ansarifar, A.; Shiah, S. F.; Bennett, M. Int J Adhes Adhes 2006, 26, 454.

23. Edwards, D. C. J Mater Sci 1990, 25, 4175.

24. Valentin, J. L.; Mora-Barrantes, I.; Carretero-Gonzalez, J.; Lopez-Manchado, M. A.; Sotta, P.; Long, D. R.; Saalwachter, K. Macromolecules 2009, 43, 334.

25. Jouault, N.; Vallat, P.; Dalmas, F.; Said, S.; Jestin, J.; Boue, F. Macromolecules 2009, 42, 2031.

26. Dugas, V.; Chevalier, Y. J Colloid Interface Sci 2003, 264, 354.

27. Pérez, L. D.; Florez, E.; Mark, J. E.; López, B. L. Polym Int 2009, 58, 811.

28. Boys, S. F.; Bernardi, F. Mol Phys 1970, 19, 553.

29. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, J. R. C. M. A.; Montgomery, J. A.; T. V. Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, G. S. M.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Pengand, C. Y.; Nanayakkara, M. A. Gaussion 03, Revision C. 02; 2003.

30. Steinberg, G. J Phys Chem 1967, 71, 292.

31. Purcell, K. F.; Drago, R. S. J Am Chem Soc 1966, 88, 919.

32. Costa, G.; Dondero, G.; Falqui, L.; Castellano, M.; Turturro, A.; Valenti, B. Macromol Symp 2003, 193, 195.

33. Castellano, M.; Falqui, L.; Costa, G.; Turturro, A.; Valenti, B.; Castello, G. J Macromol Sci B Phys 2002, 41, 451.

34. Steiner, T. Angew Chem Int Ed 2002, 41, 48.

35. Beckmann, J.; Grabowsky, S. J Phys Chem A 2007, 111, 2011.

36. Fredericks, S. Y.; Jordan, K. D.; Zwier, T. S. J Phys Chem 1996, 100, 7810.

37. Paddison, S. J.; Kreuer, K.-D.; Maier, J. Phys Chem Chem Phys 2006, 8, 4530.

38. Ambler, M. R. J Polym Sci A Polym Chem 1973, 11, 1505.

39. Hourston, D. J.; Song, M. J Appl Polym Sci 2000, 76, 1791.

40. Hourston, D. J.; Song, M.; Hammiche, A.; Pollock, H. M.; Reading, M. Polymer 1997, 38, 1.

41. Essawy, H.; El-Nashar, D. Polym Test 2004, 23, 803.