

SUPPORTING INFORMATION

In situ sol-gel obtained silica-rubber nanocomposites:  
influence of the filler precursors on the improvement of  
the mechanical properties.

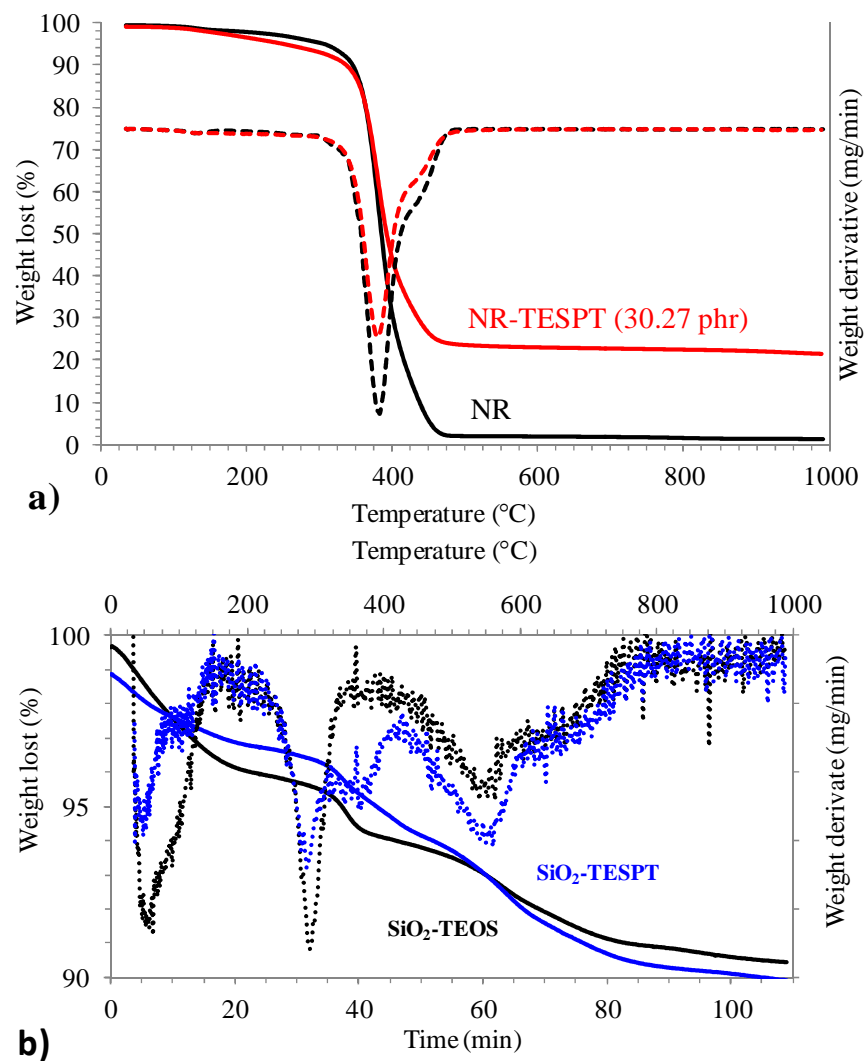
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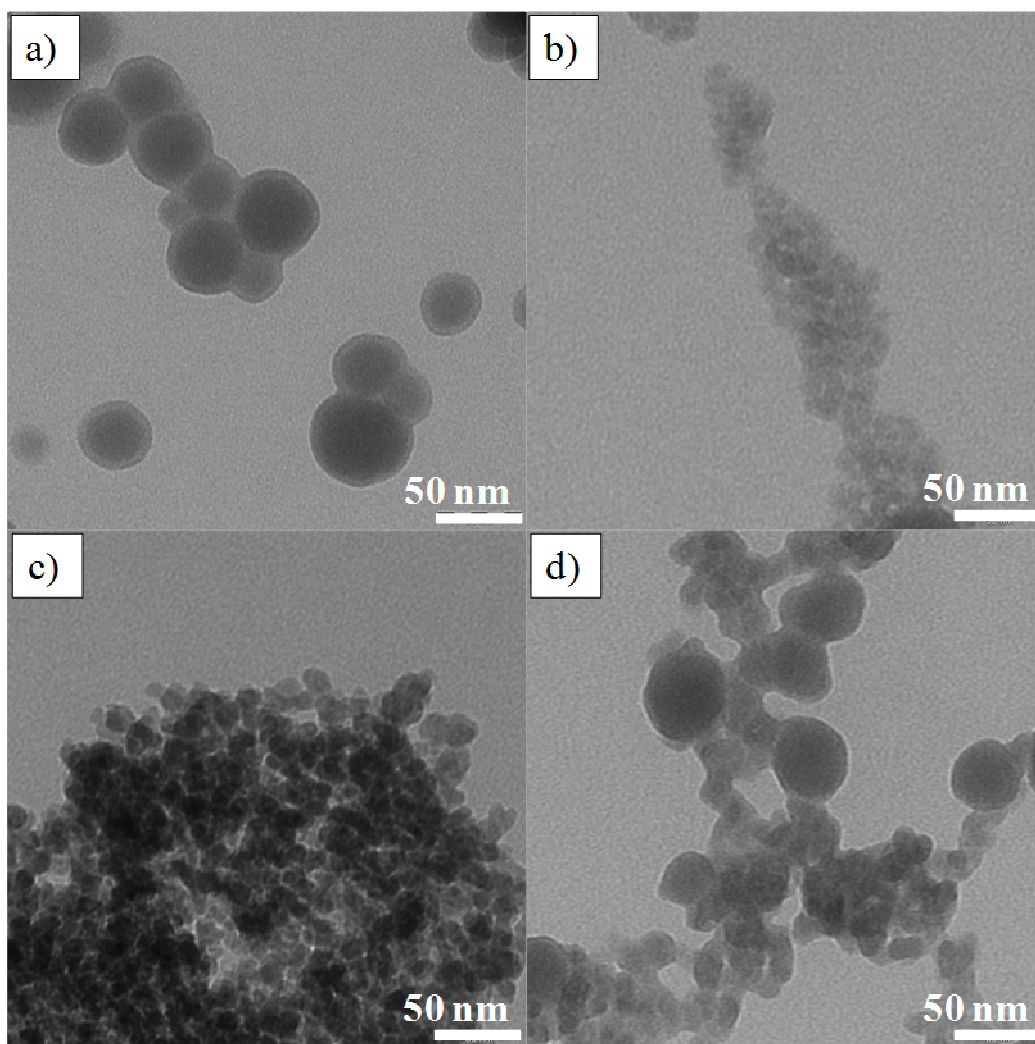
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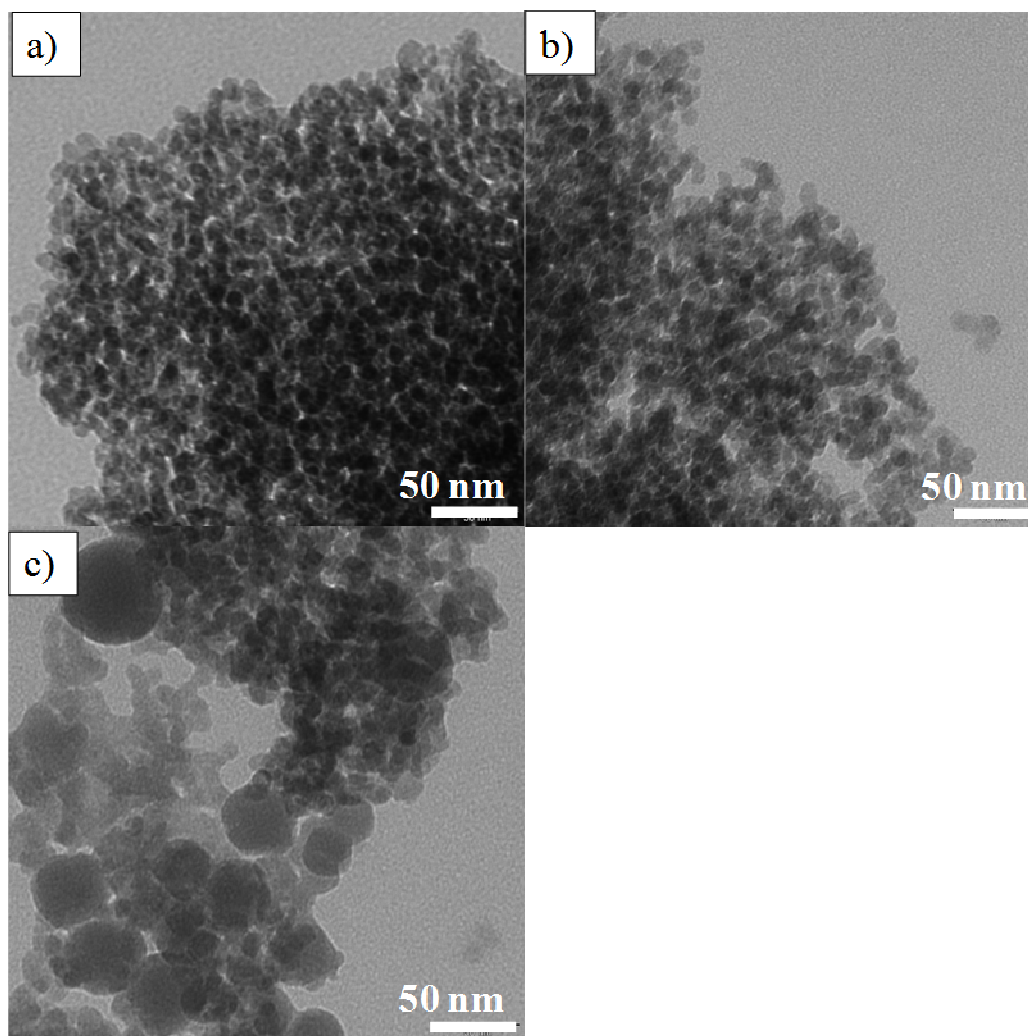
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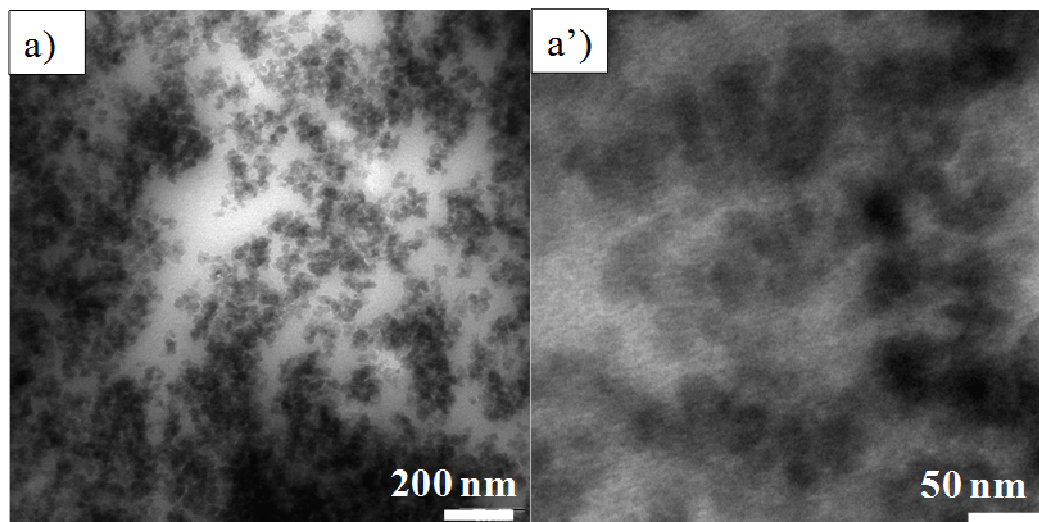
**Figure S1:** Comparison of TGA profiles and related derivatives curves of a) natural rubber (NR) and NR- TESPT composites in air flow and b) SiO<sub>2</sub>- TESPT and SiO<sub>2</sub>- TEOS powders in nitrogen flow.



**Figure S2:** TEM image of a) SiO<sub>2</sub>-APTEOS, b) SiO<sub>2</sub>-CPTEOS, c) SiO<sub>2</sub>-ICPTEOS and d) SiO<sub>2</sub>-NXT powders.



**Figure S3:** TEM images of a)  $\text{SiO}_2$ -VTEOS, b)  $\text{SiO}_2$ -PTEOS and c)  $\text{SiO}_2$ -OCTEOS powders.

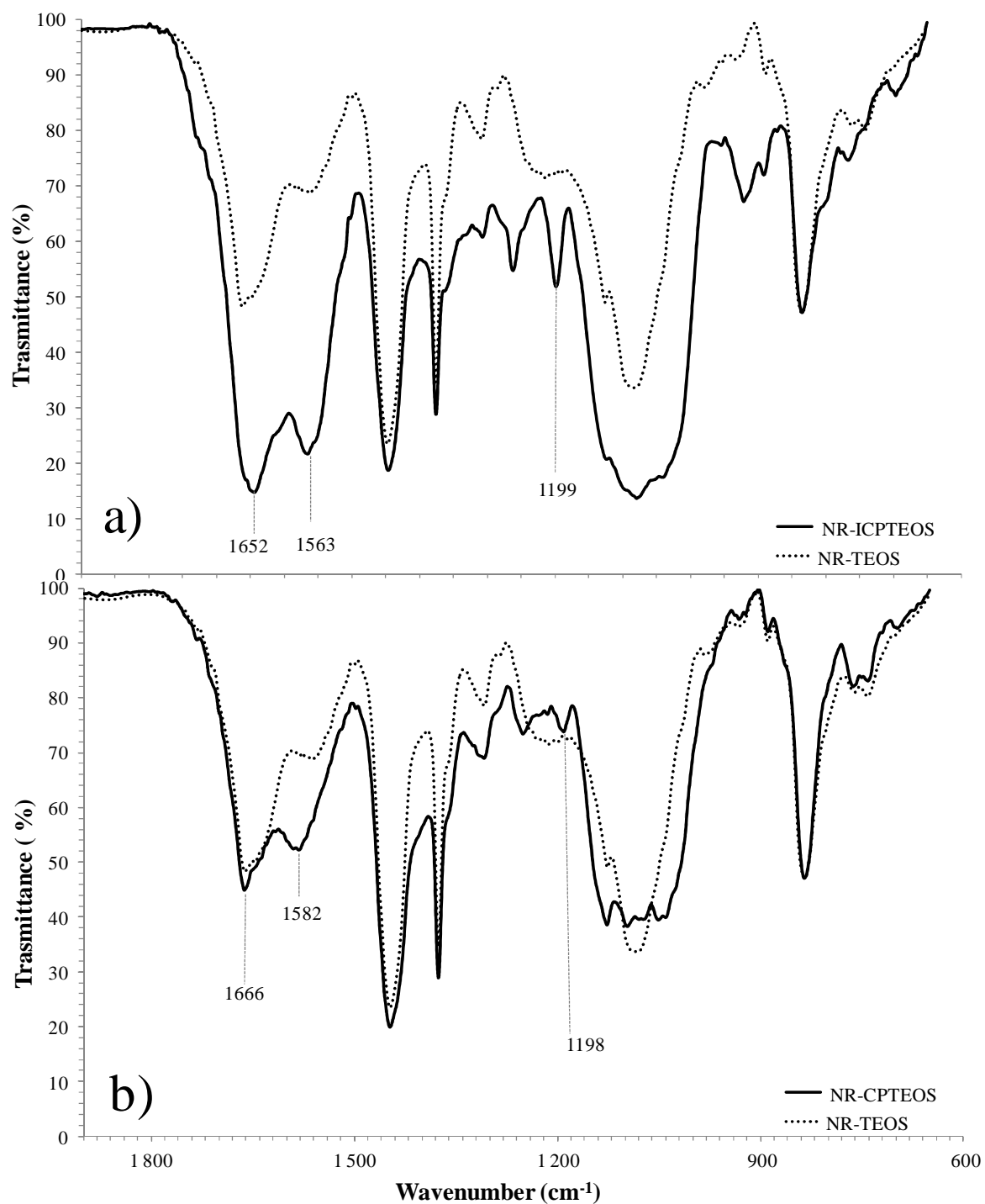


**Figura S4:** TEM image of NR-SiO<sub>2</sub> masterbatch used as a reference sample.

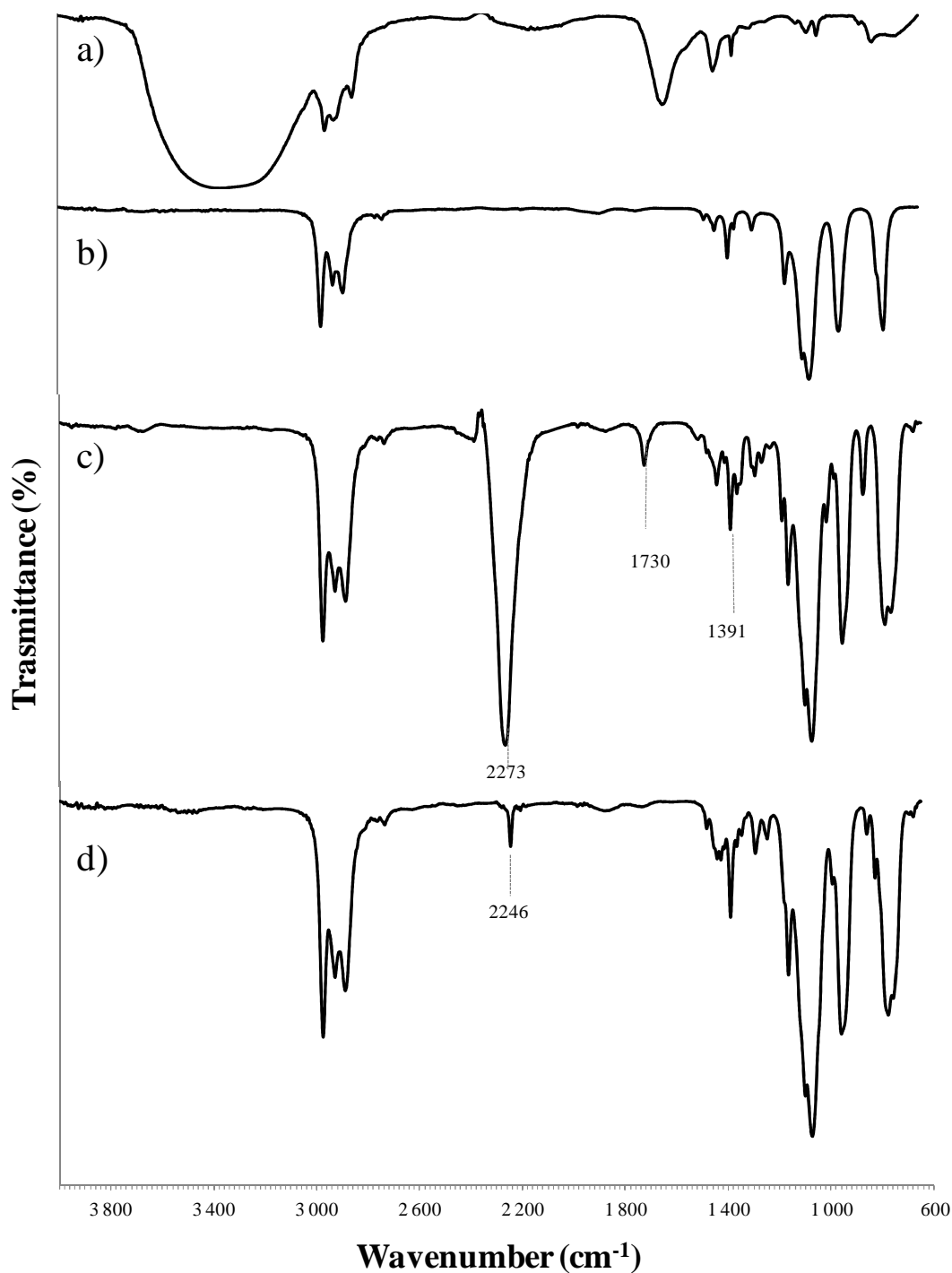
### ATR-FTIR analysis

ATR-FTIR spectra collected on suspensions of NR latex and suitable amounts of TEOS, ICPTEOS and CPTEOS precursors ( $\text{H}_2\text{O}/\text{silane}$  molar ratio = 2) after the same thermal treatment ( $70^\circ\text{C}$  for 1 h) of the synthesis conditions are reported in Fig. S5. References spectra of NR and of pure silanes, TEOS, ICPTEOS and CPTEOS were also recorded (Figure S6)

FTIR analysis demonstrated that the functional groups  $-\text{NCO}$  and  $-\text{CN}$  of NR-ICPTEOS and NR-CPTEOS easily hydrolyze in the latex basic solution, forming carbamate and carboxylate groups, respectively. This is evidenced by: a) the disappearing in NR-ICPTEOS of the  $\text{N}=\text{C}=\text{O}$  asymmetric and symmetric stretching bands at  $2273$  and  $1391\text{ cm}^{-1}$  and of the  $\text{CO}$  stretching band at  $1730\text{ cm}^{-1}$  of the precursor ICPTEOS (Figure S6c); b) the presence in NR-ICPTEOS of new bands ascribed to carbamate group: at  $1652\text{ cm}^{-1}$  the band of  $\text{CO}$  asymmetric stretching and  $1563\text{ cm}^{-1}$  of  $\text{C-N-H}$  bending, partially superimposed to the bands of the hydrolyzed silicon alkoxyde groups; at  $1199\text{ cm}^{-1}$  the band of  $\text{C-N}$  stretching of carbamate group (Figure S5a). Regarding NR-CPTEOS, the hydrolysis of  $-\text{CN}$  group is evidenced a) by the disappearance in NR-CPTEOS of the  $\text{CN}$  stretching band at  $2264\text{ cm}^{-1}$  of the precursor (Figure S6d) and b) by the presence in NR-CPTEOS of a new band of the  $\text{CO}$  stretching at  $1582\text{ cm}^{-1}$  ascribed to carboxylate group (Figure S5b) even if cannot also be excluded the formation of a small amount of amide due to the presence of a small band at  $1198\text{ cm}^{-1}$  due to  $\text{C-N}$  stretching (Figure S5b).



**Figure S5:** FTIR spectra of a suspension of NR with a) ICPTEOS and b) CPTEOS ( $H_2O/silane$  molar ratio = 2) after the same treatment ( $70^\circ C$  for 1 h) of the sol-gel synthesis. FTIR spectra are compared with that of a suspension of NR and TEOS under the same conditions (dotted lines).



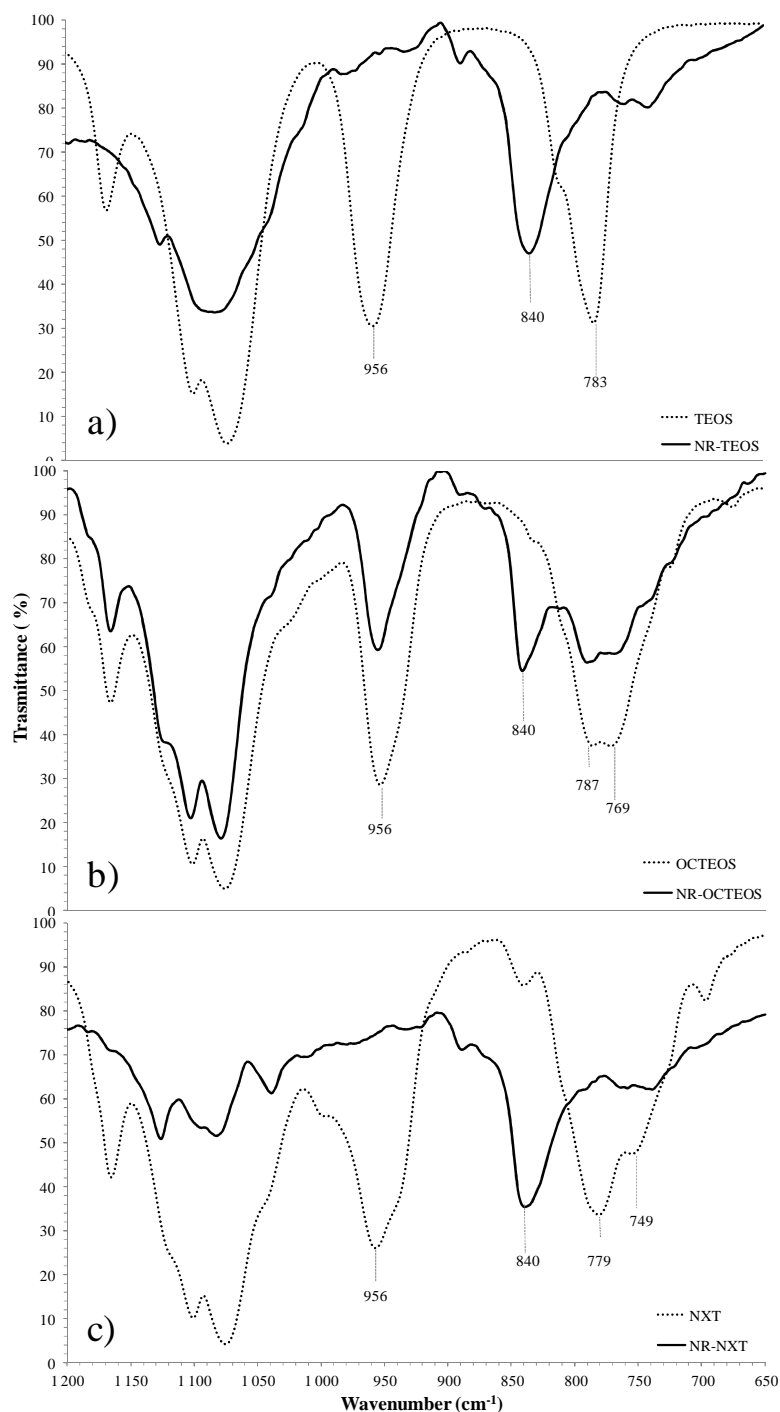
**Figure S6:** FTIR spectra of pure reagents: a) NR latex; b) TEOS; c) ICPTEOS and d) CPTEOS.

ATR-FTIR spectra (range 600-1200  $\text{cm}^{-1}$ ) of NR latex suspensions and of suitable amounts of TEOS, OCTEOS and NXT precursors ( $\text{H}_2\text{O}/\text{silane}$  molar ratio = 2), taken after the same treatment ( $70^\circ\text{C}$  for 1 h) as the *in situ* synthesis, are reported in Fig. S7 and compared with the spectra of the silanes before the reaction (FTIR spectra of the other substituted silanes are not reported).

The spectra demonstrated that after 1 hour of reaction at  $70^\circ\text{C}$  the ethoxy groups of the OCTEOS only partially reacted, unlike TEOS and the other substituted silanes which completely hydrolyzed.

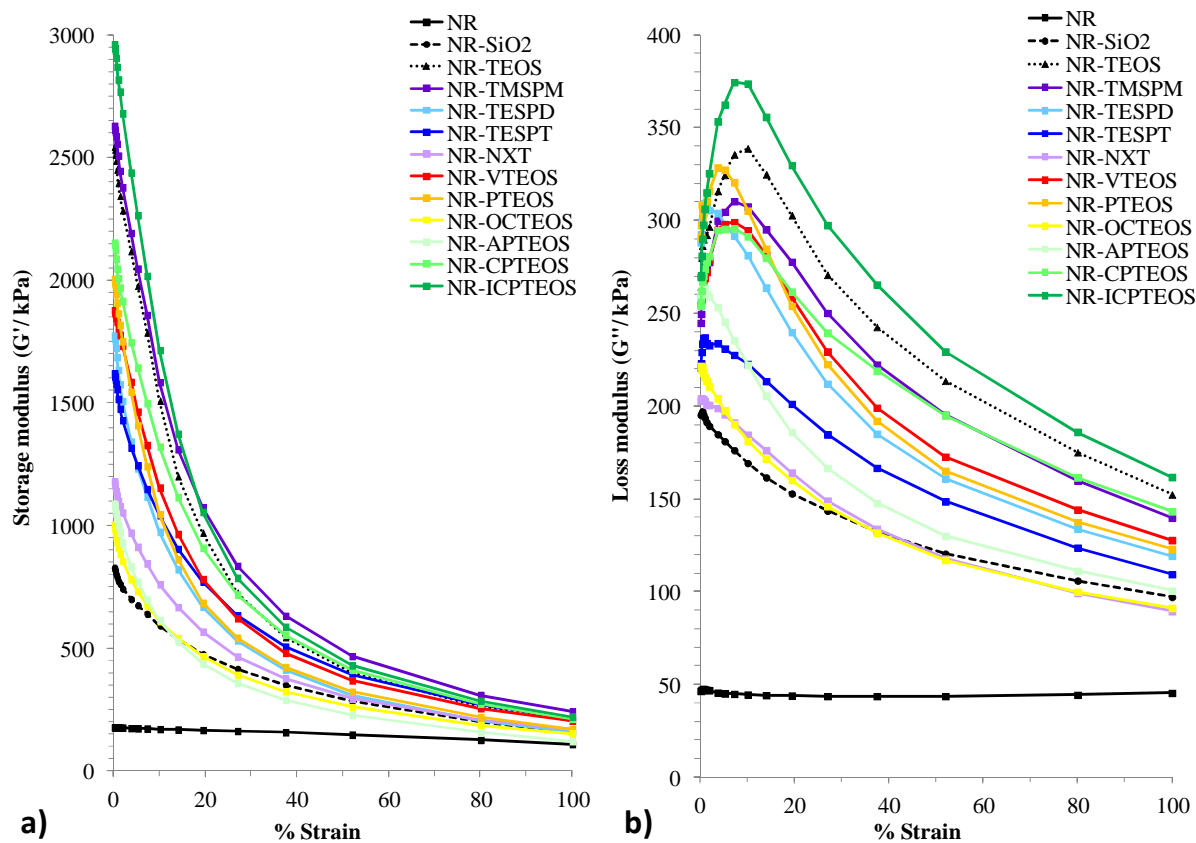
In details, TEOS spectra recorded after reaction, showed that the bands related to ethoxy groups, the (Si-O + C-O) stretching at  $783\text{ cm}^{-1}$  and the ( $\text{H}_3\text{CC}$  or  $\text{H}_2\text{CO}$ ) bending at  $956\text{ cm}^{-1}$ , are completely absent, while the band at  $840\text{ cm}^{-1}$ , due to the symmetric stretching (C-C + C-O) of the ethanol, which is a product of the hydrolysis/condensation reaction is easily detectable (Figure S7 a).

In the case of OCTEOS, the same bands of the alkoxy groups at  $787\text{ cm}^{-1}$  and  $956\text{ cm}^{-1}$  were still present after the reaction, though less strong and superimposed to the ethanol band at  $840\text{ cm}^{-1}$  (Figure S7 b). Regarding NXT, the behavior is similar to that of TEOS. The alkoxy groups at  $779\text{ cm}^{-1}$  and  $956\text{ cm}^{-1}$  disappeared after reaction, and the ethanol band at  $840\text{ cm}^{-1}$  was detectable (Figure S7 c).



**Figure S7:** FTIR spectra of a suspension of NR and a) TEOS, b) OCTEOS and c) NXT ( $\text{H}_2\text{O}/\text{silane}$  molar ratio = 2) after the same treatment ( $70^\circ\text{C}$  for 1 h) of the sol-gel synthesis (bold lines). FTIR spectra are compared with those of silanes before reaction (dotted lines).





**Figure S8:** a) Storage modulus  $G'$  and b) loss modulus  $G''$  after the thermal treatment at  $150^{\circ}\text{C}$  of the uncured *in situ* silica-rubber composites NR-TMSPM, NR-TESPD, NR-TESPT, NR-NXT, NR-VTEOS, NR-PTEOS, NR-OCTEOS, NR-APTEOS, NR-CPTEOS, NR-ICPTEOS compared with NR-SiO<sub>2</sub> and pure NR.