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Effect of coupling agent on the morphological characteristics of natural rubber/silica composites foams

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Abstract: The effect of coupling agent on the morphological characteristics of natural rubber/silica composite foams with various silica contents was studied. Bis 3-triethoxysilylpropyl tetrasulfide (TESPT) was used as coupling agent in this system. It could make a chemical bond with the silica particles. By increasing the silica content, cell size of foams was reduced more that 50% and foam density was increased up to 40%. However, compatibilized composites demonstrated about 20% lower foam density and higher cell size. In this case, strong adhesion between the components prevented gas from escaping out. While, in the foams excluded coupling agent the weak adhesion between particles and rubber created an escape path for gas from the interface of components. So, lower cell size and higher density were achieved.

Keywords: natural rubber; foam; silica, coupling agent; cell morphology

1 Introduction

Rubber foams have higher flexibility than thermoplastic foams and they are more interested in several applications such as thermal insulation, transportation and energy absorption. The properties of rubber foams depend on the cell morphology and density, which in turn, depend on the condition of foaming (1). The control of morphology in the rubber foams is more difficult than thermoplastic foams because the curing and foaming progress, simultaneously (2-5). In chemical foaming method, since gas generation and curing reaction progress by heating, the suitable heating conditions can be identified, comparatively (6).

Natural rubber has unique properties such as high flexibility at low temperatures, high tear strength, impact resistance and resilience (7). Some researches have been conducted on the preparation and properties of natural rubber foams (8). The effect of temperature of foaming on the cell morphology and acoustic efficiencies of NR foams was studied. The NR foam with lower cell size exhibited the largest sound absorption coefficient value. Ariff et al. investigated the effect of rubber viscosity on the properties of natural rubber foams (9-11). Pechurai et al. studied the effect of 4,4'-oxydibenzenesulfonyl hydrazide (OBSH) blowing agent content on the cure characteristics, mechanical and morphological properties of NR foams (12). The effect of concentration of sodium bicarbonate and azodicarbonamide as blowing agents on the cell morphology of natural rubber foam was also studied in separate works (13,14). At high concentration of blowing agent, the coalescence between bubbles was observed owing to high gas content in the rubber matrix (14). Some studies focused on the preparation and properties of NR composite foams. The influence of carbon black on the morphology and properties of this kind foam was demonstrated. Another work has been performed on the NR/wood flour composite foams (15). In these works, the mechanical properties of NR composite foams were investigated.

Silica has been used as an important reinforcing agent in a rubber compound together with carbon black (16-19). Silica has a polar structure which results in strong filler–filler interactions. This property can cause a poor adhesion of silica to rubber matrix. In general, silane coupling agent is used in order to improve the filler dispersion (20,21). Most of studies on the improved interfacial compatibility were conducted by the goal of improving mechanical properties. However, the effect of interfacial adhesion on the cell morphology of rubber foams was not studied, yet. In this work, the cell morphology of natural rubber/silica

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composite foams affected by the presence of coupling agent was studied and discussed.

2 Materials and methods

2.1 Materials

Natural rubber ribbed smoked sheet 1 (RSS1) was purchased from Thomson Enterprise (India) Co. Precipitated silica (ULTRASIL VN3) was provided from Evonik Industries. Tetra methyl thiuram disulphide (TMTD), N-Cyclohexyl-2-benzothiazole sulfonamide (CBS) and activated *Azodicarbonamide* (porofor ADC/K) were purchased from Lanxess Co. Sulfur, stearic acid(SA), zinc oxide (ZnO) and paraffin oil were supplied from local companies. Bis 3-triethoxysilylpropyl tetrasulfide (TESPT), Si69 grade from Evonik was used as coupling agent.

2.2 Sample preparation

The compounding of ingredients was performed by an internal mixer (Brabender W50 EHT) in two steps. First, at 120°C natural rubber, silica and coupling agent (if included) was mixed for 6 min. The compound was discharged from the mixer. In the second step at 60°C, paraffin oil was gradually added within about 4 min. After that, stearic acid, zinc oxide, TMTD, CBS sulfur and azodicarbonamide were added to the mixer, respectively. The rotating speed and total mixing time was respectively fixed at 80 rpm and 16 min for all samples. The samples nomenclatures and compositions are presented in Table 1.

Foaming of samples simultaneously with curing was performed at 140°C and 160°C using a hot oven. After foaming, samples were cooled at room temperature.

2.3 Characterizations

FTIR spectra were taken on a Shimadzu IR-470 spectrometer. The density of foams was measured by displacement method in accordance with ASTM D792. The cell structure of foams was analyzed using a scanning electron microscope (SEM, VegaII Tescan, Czech). Before SEM tests, the samples were sputter-coated with gold for better resolution. The average cell size of the foam samples was determined from the measurements of at least 50 different cells by ImageJ software.

3 Results and discussion

3.1 FTIR analysis

Figure 1 shows the FTIR spectra of pure silica, TESPT coupling agent and silica modified with TESPT. The comparison between the spectra shows the appearance of bimodal bands at 2870 and 2930 cm^{-1} which were assigned to the aliphatic CH_3 and CH_2 groups. Also, the bands at 1450 and 1505 cm^{-1} were assigned the CH_3 groups. The presence of these bands proved the chemical bond formation between silica and TESPT. Moreover, the broad band characteristic for hydrogen-bonded silanols at 3400 cm^{-1} decreased in intensity and shifted toward higher wavenumbers to about 3440 cm^{-1} after modification.

3.2 Density measurement

The density of samples foamed at 140 and 160°C is presented in Figure 2. As seen, by increasing the silica content, the density of foam increased. At 160°C, the density of foams increased from 0.21 g/cm^3 (A0 sample)

Table 1: Formulation of prepared samples.

Ingredient/ Sample code	A0	A10	A20	A30	A40	B10	B20	B30	B40
Natural rubber	100	100	100	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2	2	2	2
Zinc oxide	4	4	4	4	4	4	4	4	4
Oil	40	40	40	40	40	40	40	40	40
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TMTD[1]	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
CBS[2]	1	1	1	1	1	1	1	1	1
Silica	0	10	20	30	40	10	20	30	40
TESPT[3]	0	1	2	3	4	0	0	0	0
Azodicarbonamide	8	8	8	8	8	8	8	8	8

[1] Tetra methyl thiuram disulphide, [2] N-Cyclohexyl-2-benzothiazole sulfonamide, [3] Bis 3-triethoxysilylpropyl tetrasulfide.

to 0.30 and 0.37 g/cm³ for A40 and B40, respectively. However, the foams included coupling agent (A series) always had lower density than ones excluded (B series). The differences between the density of A and B were intensified by increasing the silica volume. At 40 phr silica, the addition of coupling agent made lighter foam with about 20% lower density. Similar trend was observed for the foams prepared at 140°C. Just, foams produced at 160°C had about 5-20% lower density than foams produced at 140°C depending on the amount of filler.

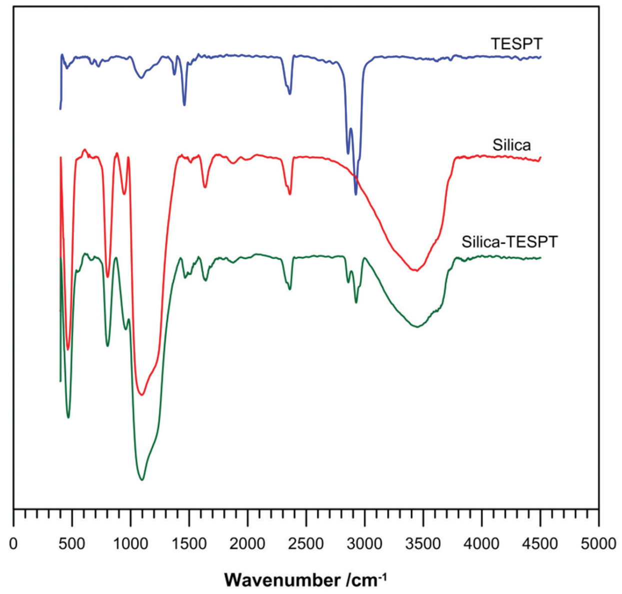

Figure 1: FTIR of neat and modified silica with bis 3-triethoxysilylpropyl tetrasulfide (TESPT).

3.3 Morphology observation

Figure 3 shows the SEM images of the foams prepared at 140°C, with and without coupling agent. By increasing the silica content, the cells became smaller and more uniform. For the sample containing low silica volume (10 phr), the cell size was between 300 to 600 micron. By increasing the silica content up to 40 phr, cell size decreased to lower than 300 micron. The cell size for the samples included TESPT was higher than samples excluded one. However, increasing silica content in both cases lowered the cell sizes and produced a more uniform distribution of cells.

Figure 4 represents the SEM images of foams prepared at 160°C. By increasing the temperature of foaming, larger cell size formed in the polymer matrix. It might be due to the higher gas generation at higher temperature or lower viscosity of polymer at higher temperature as the viscosity is a retarding force against bubble growth (22). Similar to prepared foams at 140°C, by increasing the silica filler, the cell size decreased. The variation of cell size verses silica content is shown in Figure 5. As shown, the average cell size decreased continuously by filler content. The average cell size for A0 sample foamed at 140°C was about 550 μm which was reduced for A40 to 320 μm. The B40 that did not contain coupling agent had about 50 μm lower cell size. Similar trend was observed at 160°C and the cell size reduced about 30-40% by increasing 40 phr silica. In most cases, the cell size of foams at 160°C was higher than 140°C. But when the concentration of filler was low (0, 10 or 20 phr), the results were inverse.

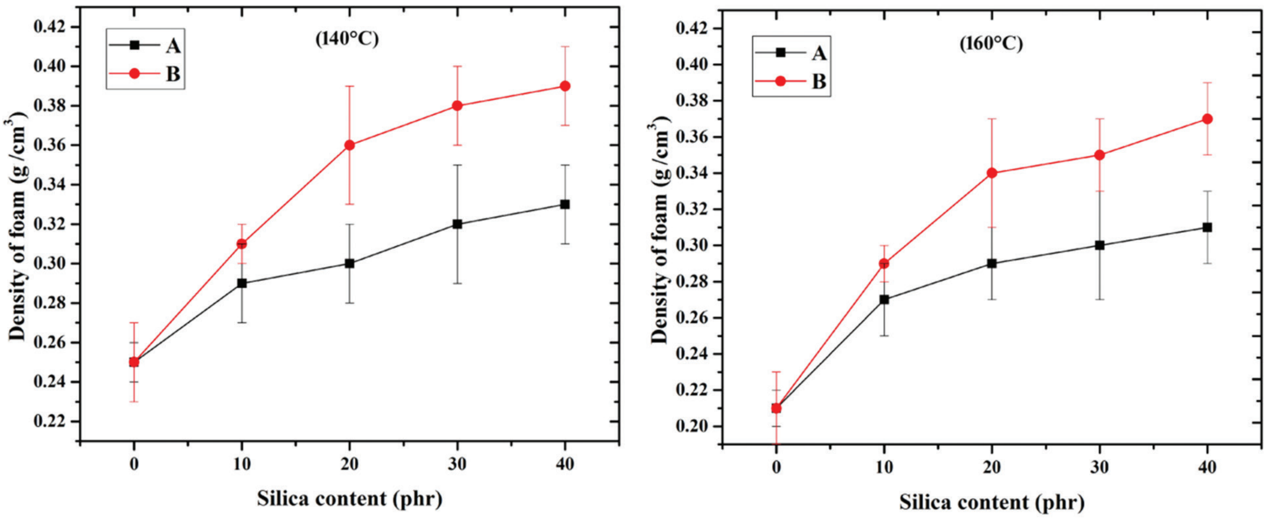

Figure 2: The density of foams prepared at different temperatures as a function of silica content: (a) coupling agent included, (b) coupling agent excluded.

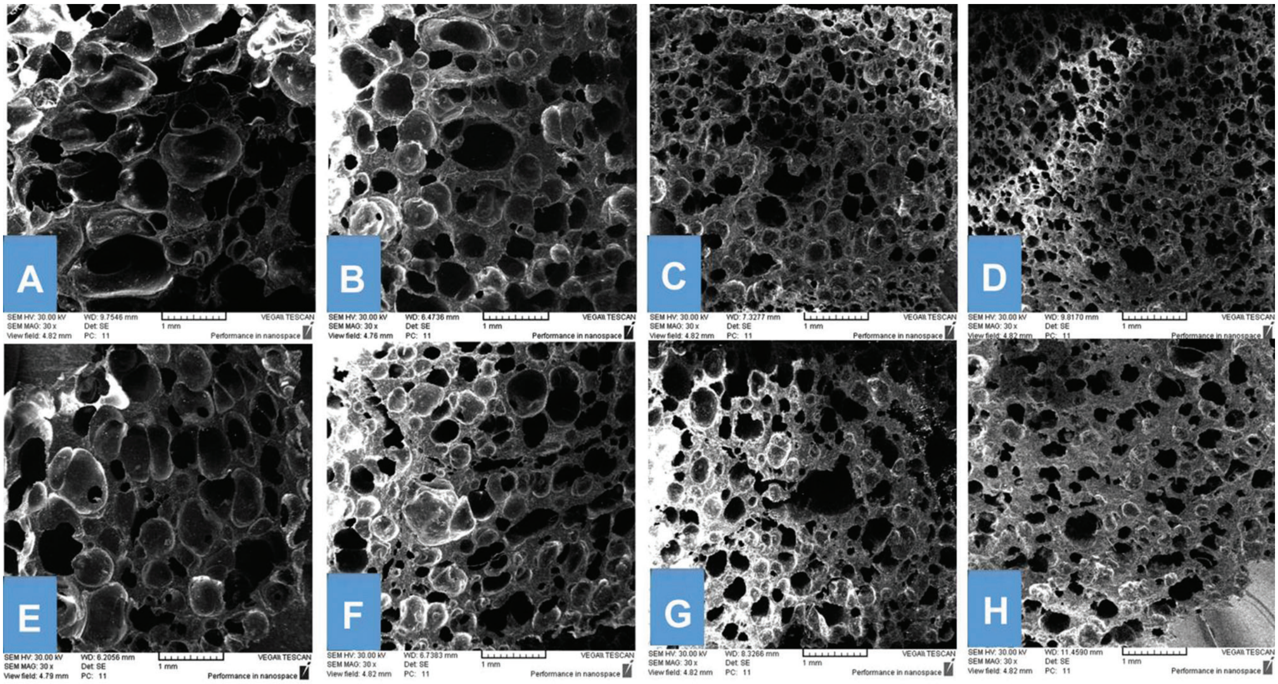

Figure 3: SEM images of foamed samples at 140°C for (a) B10, (b) B20, (c) B30 and (d) B40 and foamed samples at 160°C for (e) B10, (f) B20, (g) B30 and (h) B40.

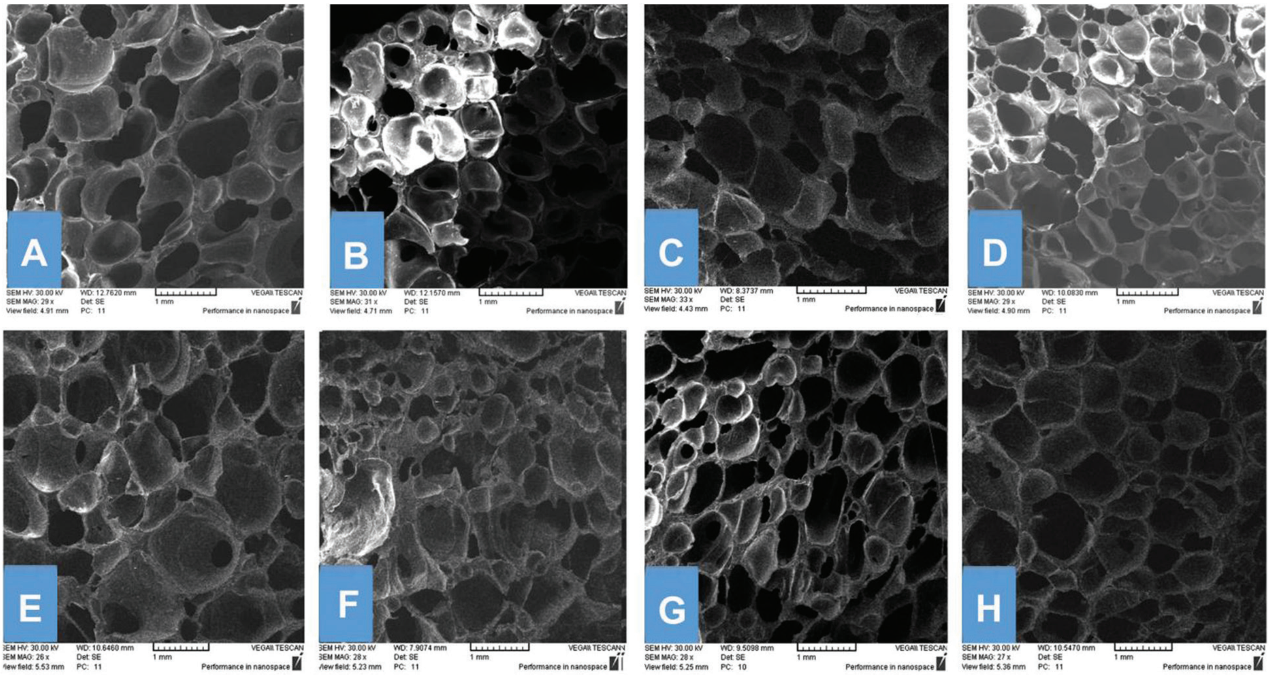

Figure 4: SEM images of foamed samples at 140°C for (a) A10, (b) A20, (c) A30 and (d) A40 and foamed samples at 160°C for (e) A10, (f) A20, (g) A30 and (h) A40.

Actually, the role of temperature in thermoset foams is very complicated (23,24). Increasing the temperature reduces the viscosity and accelerates the blowing agent decomposition that cause to speed up the bubble growth. On the other hand, higher temperature results in faster curing reaction which stop the growth of bubble. It seems

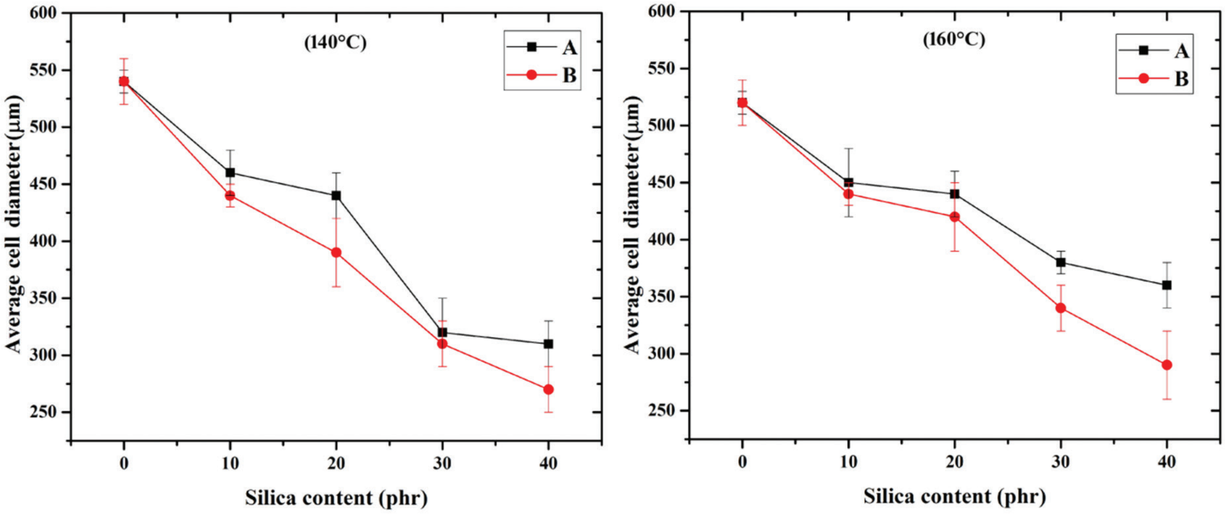

Figure 5: The variation of average cell diameter of foams as a function of silica content at different foaming temperature.

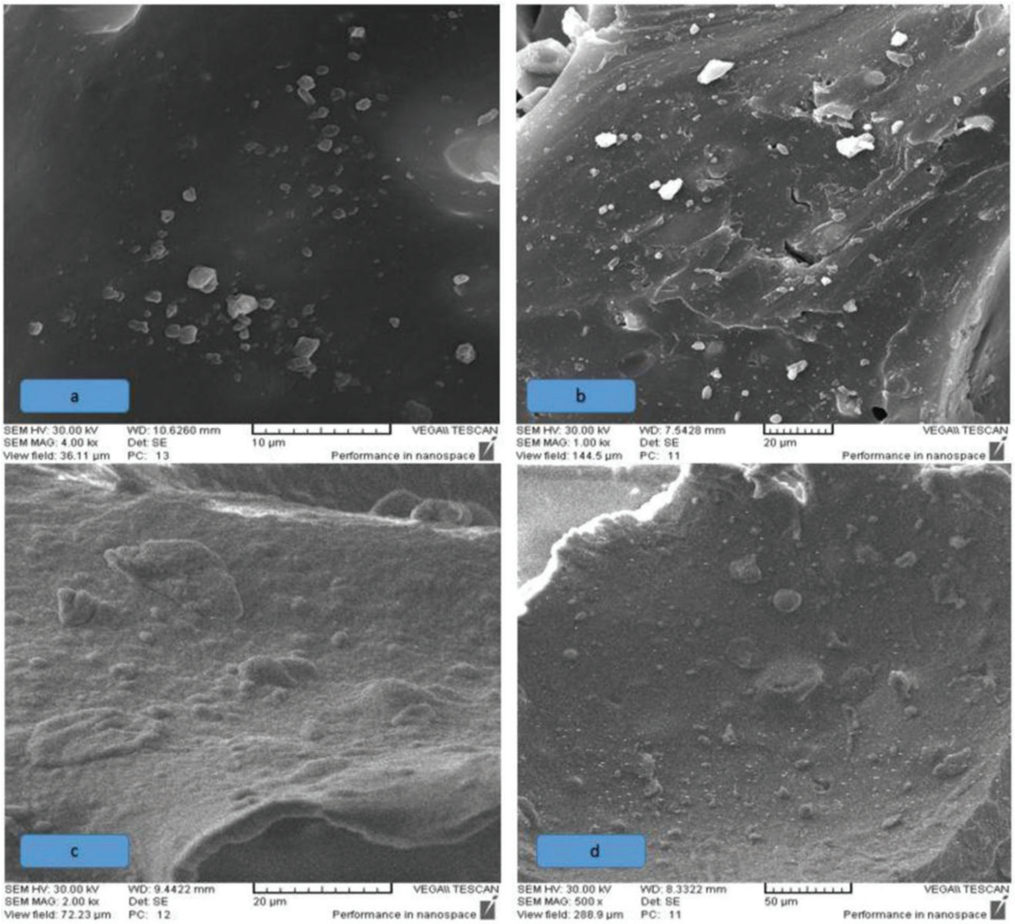

Figure 6: SEM images of cell walls of (a) B10, (b) B30, (c) A10 and (d) A30.

that in the foams with large bubble size (like A0, A10 and B10) bubble growth stage consumed more time. In these cases, increasing the temperature, accelerated the curing reaction and stopped the growth of bubble before it was stopped, thermodynamically. So, the bubble size was decreased by increasing the temperature. But, in the foams with smaller bubble size (A40, B40), increasing the temperature, facilitated the bubble growth by reducing the viscosity or accelerating the blowing agent decomposition. However, when the coupling agent included in the formulation, the cell size was higher. Comparing the A40 and B40 displayed about 50 and 100 μm higher cell size of A40 foamed at 140 and 160°C, respectively.

The SEM images from inter cells of different foams were taken to understand the effect of coupling agent on the morphology and is presented in Figure 6. As seen, in sample B10 and B30 (Figures 6a and 6b) the filler particles were clearly observed which were not covered with the rubber matrix. Some micro cracks were also observed in the sample B30 containing higher filler concentration. These were related to the poor adhesion between filler particles and rubber matrix when coupling agent excluded. While, when coupling agent was used, no free particle was observed in the SEM images. Figures 6c and 6d show the cell walls of A10 and A30, respectively. It was observed that the filler particles completely were covered by rubber matrix which was attributed to the good affinity between filler and rubber in the presence of coupling agent. In this case, strong adhesion between the components prevented gas from escaping. So foam cells became larger. While in BX (B10, B20, B30 and B40) samples, the weak adhesion between particles and rubber created an escape path for gas from the interface of them. So, lower cell size and higher density were obtained in the foams excluded coupling agent.

4 Conclusions

In this work, the effect of coupling agent on the morphology of natural rubber/silica composite foams with various silica contents was studied. FTIR analysis illustrated chemical bond formation between silica particle and Bis 3-triethoxysilylpropyl tetrasulfide (TESPT) coupling agent. Increasing the silica content lowered the cell size and produced a more uniform cell distribution. The cell size of foams was reduced about 30-40% by increasing 40 phr silica. Foams produced at 160°C had about 5-20% lower density than foams produced at 140°C depending on the amount of filler. However, compatibilized composites demonstrated lower foam density and higher cell size due to strong adhesion between the components that prevented gas from escaping out of cells during bubble growth. While, in the foams excluded coupling agent the weak adhesion between particles and rubber created an escape path for gas molecules from the interface of them. So, lower cell size and higher density were obtained.

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