Bull. Mater. Sci. (2019) 42:176
https://doi.org/10.1007/s12034-019-1867-4

Silica- and diatomite-modified fluorine rubber nanocomposites

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MS received 18 May 2018; accepted 8 February 2019; published online 30 May 2019

Abstract. To find the most suitable filler system for fluorine rubber, a simple and green method to introduce a limited content of silanol groups on the surfaces of silica and fluorine rubber was studied. Fluorine rubber nano-composites were prepared by using nano-silica, diatomite and carbon black as the reinforcement and filler and the coupling agents KH550, KH590 or Si69 as the compatibilizer between the filler and fluorine rubber. The structure and morphology of the composites were investigated by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The results showed that the most suitable filler system for fluorine rubber was the diatomite and silica compound (8:12 mass ratio), the best coupling agent was KH550 at 2 parts per hundred rubber (phr). The modified compound filler was silanized with the coupling agent KH550 for fluorine rubber by FTIR analysis, the compatibility between the filler and fluorine rubber was improved by SEM analysis and further confirmed by thermogravimetric analysis to improve the thermal properties of fluorine rubber with the filler compound system.

Keywords. Fluorine rubber; coupling agents; mechanical properties; thermal properties.

1. Introduction

With the wider application of fluorine rubber products, people's demand for fluorine rubber products is growing more and more, but the mechanical properties of pure fluorine rubber are poor. To solve this problem, fillers, such as carbon black and silica, were used to improve the mechanical properties of fluorine rubber [1], but the carbon black causes industrial pollution during the production process and the reinforced effect of silica was not ideal. In view of this problem, attempts were made to find a natural non-polluting material [2] to improve the properties of fluorine rubber. At present, some scholars have filled pure natural diatomite in various kinds of rubbers and the effect of modification is not significant [3]. In this work, a new, simple and green methodology to introduce a limited content of silanol groups on the surfaces of the silica and diatomite compound filler and fluorine rubber was studied to find the most suitable filler system for fluorine rubber and the modified fluorine rubber nanocomposites were prepared by using diatomite [4,5], carbon black and silica [6,7] as the reinforcement and filler and the coupling agents KH550, KH590 or Si69 [8] as the compatibilizer between the filler and fluorine rubber. The diatomite used is in disc shape with a very large specific surface area. Due to its porous structure, it is more suitable for rubber immersion [9,10]; moreover, the diatomite and silica [11] do not cause pollution in the process of production and can also improve the properties of the rubber. Therefore, the authors used diatomite and silica (or carbon black) to modify fluorine rubber and the coupling agent KH550 was used as the compatibilizer between the fillers [12] and fluorine rubber.

2. Experimental

2.1 *Materials*

Fluorine rubber (FKM, FE2602-1, copolymer of vinylidene fluoride and perfluoropropylene, T_g: 20°C) was purchased from Shanghai 3F New Materials Co. Ltd (China). Silica (A 200, industrial grade, size: 7–40 μm, Shanghai Deyude Trade Co. Ltd) was obtained from Shanghai Deyude Trade Co. Ltd (China). Diatomite (industrial grade, 10–20 $m^2\,g^{-1}$ of specific surface area) was supplied by Beijing Chuangqingyuan Filter Equipment Co. Ltd. Carbon black (grade N330) was purchased from Tianjin Tianyi Century Chemical Products Technology Development Co. Ltd. KH550 (3-aminopropyltriethoxysilane), KH590 (3-mercaptopropyl trimethoxysilane), Si69 (double-(γ-triethoxy silicon propyl)tetrasulphide) and $3^{\#}$ curing agent (N,N'-dicinnamylidene-1,6-hexanediamine) were purchased from Zigong Tianlong Chemical Co. Ltd (China). All other agents were commonly available commercial materials (China).

2.2 *Composite preparation*

Firstly, the diatomite and silica were washed with distilled water at 60°C to remove impurities from the hole and then with

Table 1. Experimental formulation (mass).

Formulation	FKM	Fillers	MgO	Accelerant M	Sulphur	$3^{\#}$ vulcanizing agent	$Ca(OH)_2$
phr	100	20	3	2.5	1	2	4

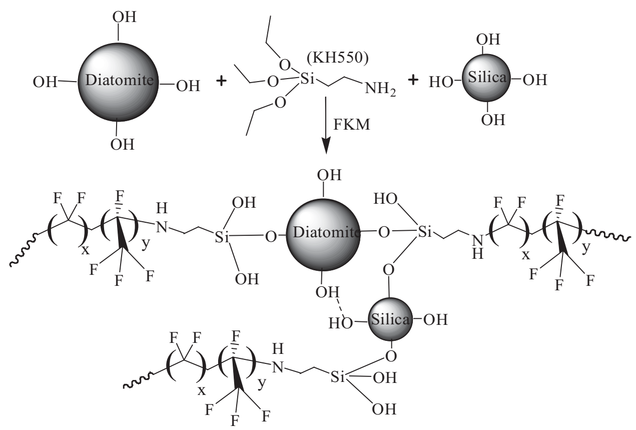

Figure 1. Schematic illustration of the preparation of filler-modified FKM nanocomposites.

20% sulphuric acid solution under ultrasonication to remove metal and non-metal oxides, filtered and dried, and treated at 400°C to remove organic impurities. Thereafter, the diatomite and silica were treated with the modifier KH550 (KH590 or Si69) with mechanical stirring at 60°C for 2 h and dried in an oven at 50°C.

FKM was masticated for 30 min on a XK-160 two-roll mill (Shanghai first rubber machinery) with a nip gap of 1 mm and a set temperature of 60°C. Then, the distance between the two rolls was adjusted up to 4 mm. The mixed-FKM was prepared by adding masticated-FKM, silanized diatomite and silica and other agents as shown in table 1. Finally, the mixtures were cured for 30 min in an electrically heated hydraulic press (XLB-D 350 × 350 × 2, Shanghai first rubber machinery) at 170°C under a pressure of 10 MPa. The post-curing process involved placing the samples in an ageing box (401B, Jiangdu Test Mechanical Ltd.) at 200°C for 2 h.

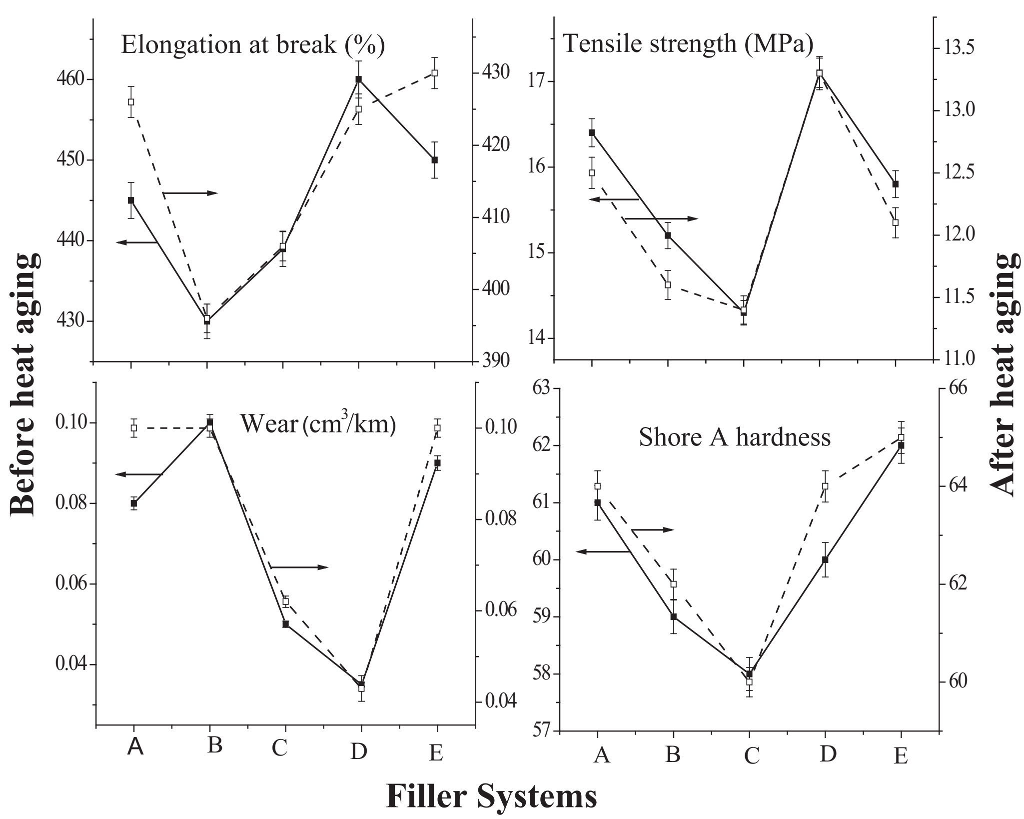

Figure 2. Effect of the filler on the mechanical properties. Notes: A: 20 phr carbon black; B: 20 phr silica; C: 20 phr diatomite; D: 10/10 diatomite/silica and E: 10/10 carbon black/diatomite.

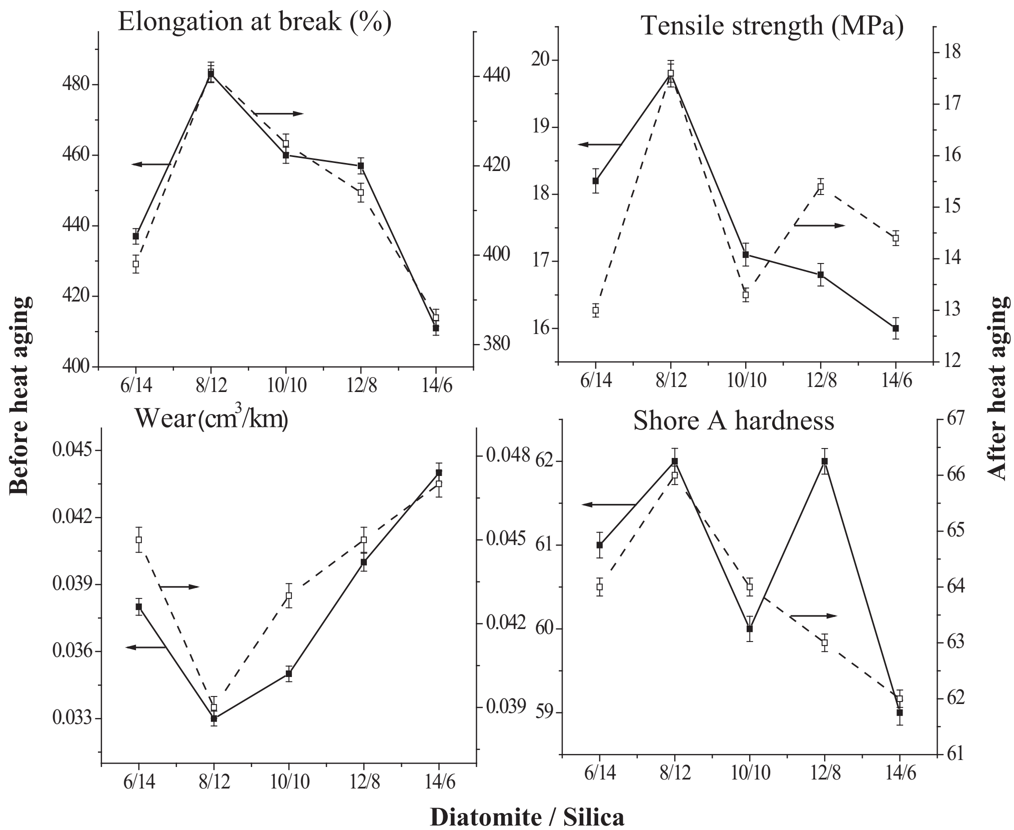

Figure 3. Effect of content of silica and diatomite compound on the mechanical properties.

The schematic illustration of the preparation of the silica and diatomite compound filled-FKM nanocomposites is shown in figure 1.

2.3 *Characterization*

The mechanical properties of the nanocomposites, such as tensile strength and elongation at break, were determined by a universal testing instrument (model CSS-2200, Zhongji Application Technical Institute, China) with a strain rate of 100 mm min^{-1} according to the ASTM D638 method. Shore A hardness was measured on 6 mm thick samples, according to ISO 7619:1997. Wear attrition was determined according to BS903A9 using an Akron machine (MN-74). Heat ageing of the samples was measured according to ISO 188-1998. For each of the measurements, an average of at least five readings was taken. Errors in the measurement of the mechanical properties were within 10%.

2.3a *FTIR spectroscopy*: The infrared spectra of the samples were recorded using an Fourier-transform infrared (FTIR) spectrometer (model SPECTRUM 2000, Perkin Elmer Co., USA). FTIR spectra were collected after 256 scans at a resolution of 2 cm^{-1} in the region of 4000–400 cm^{-1}.

2.3b *SEM*: The fluorine rubber nanocomposite samples were fractured in liquid nitrogen; then the fracture surface was sputtered with gold and the fracture morphology of the samples was observed by scanning electron microscopy (SEM) (model S-4300, Hitachi Co. Japan).

2.3c *TG analysis*: The samples were cut into slices of size of $5 \times 5 \times 1$ mm^3 and tested with a thermogravimetric (TG) analyser (Netzsch Co. Ltd., STA449F3 Jupiter, Germany) from 50 to 550°C using a heating rate of 5°C min^{-1} in an atmosphere of nitrogen.

3. Results and discussion

3.1 *Effect of different filler systems on mechanical properties of fluorine rubber nanocomposites*

The effect of different filler systems on the properties of fluorine rubber nanocomposites is presented in figure 2. The mechanical properties were the best for the fluorine rubber filled with diatomite and silica; this may be the reason why the diatomite had a larger particle size, larger specific surface and more holes compared with silica and carbon black and could

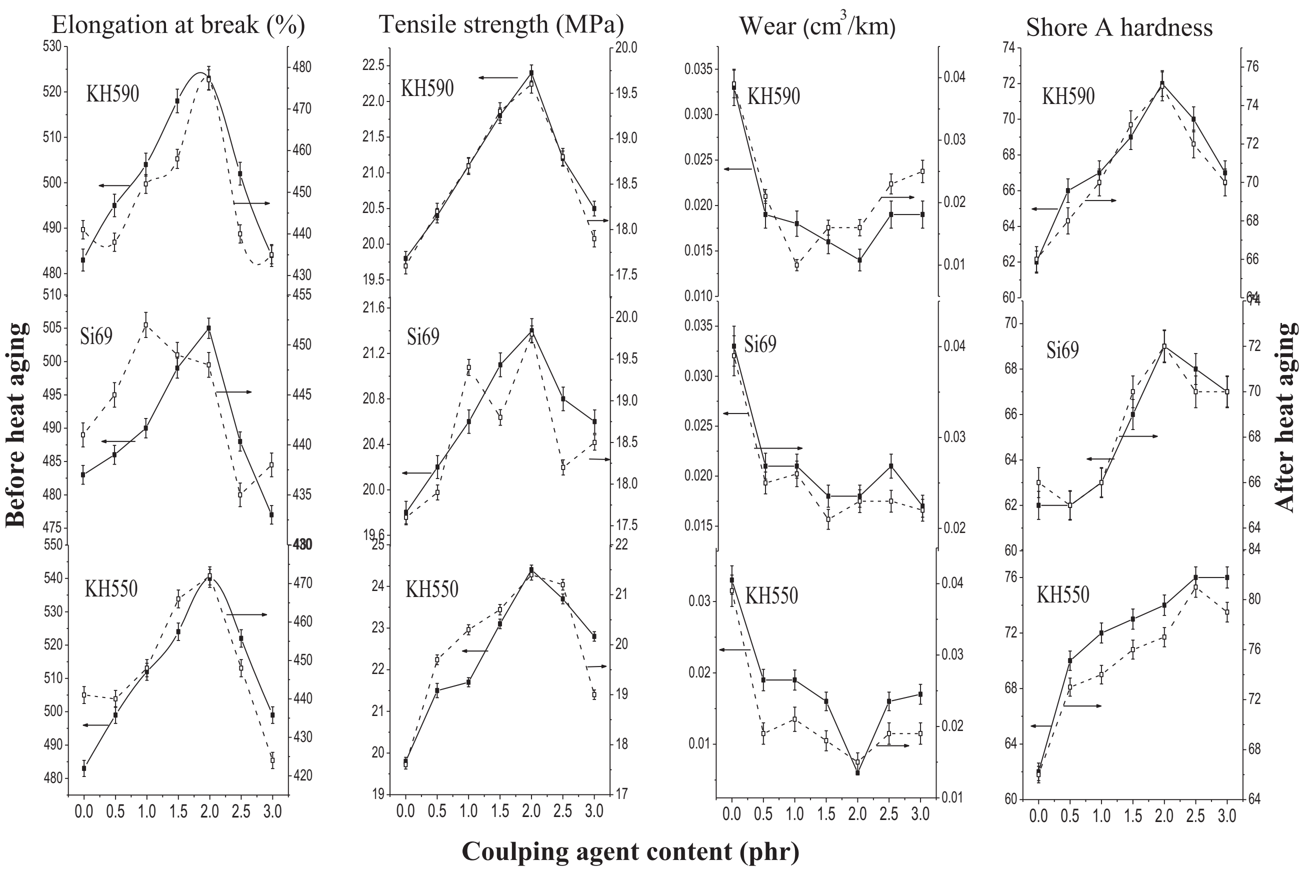

Figure 4. Effect of the coupling agent on the mechanical properties of diatomite-filled FKM vulcanizates.

adsorb more rubber. On account of the larger particle size of diatomite, a little quantity of rubber also was not adsorbed; therefore, some fillers with a smaller particle size were needed for the reinforcement of fluorine rubber. The chemical composition of the diatomite and silica is SiO_2; the effect of the diatomite and silica compound was the best according to the theory that similar chemical materials dissolved mutually.

3.2 *Effect of filler content on mechanical properties of fluorine rubber nanocomposites*

To study the effect of different diatomite contents on the mechanical properties of fluorine rubber nanocomposites, the mass ratio of the diatomite and silica compound was studied and the results are shown in figure 3. With the addition of silica, the mechanical properties of the fluorine rubber nanocomposites first improved and then declined, and the mechanical properties were best when the diatomite/silica ratio was 8:12. It could be considered that the addition of silica resulted in an increase in the contact area and in the compatibility between the filler and fluorine rubber nanocomposites and thereby improved the mechanical properties. However, when the silica content was more than 12 parts per hundred rubber (phr), uniform dispersion of silica in the rubber becomes difficult because of its smaller size and the mechanical properties were declined. Therefore, the best mass ratio of the diatomite and silica compound was 8:12.

3.3 *Effect of coupling agent on mechanical properties of silica and diatomite compound filler-modified FKM nanocomposites*

As the effect of pure natural diatomite-modified rubber was not significant, a new, simple and green methodology to introduce a limited amount of silanol groups on the surfaces of diatomite and fluorine rubber was studied by using the coupling agents KH550, KH590 or Si69 as the compatibilizer between the filler and fluorine rubber. The effect of the coupling agent on the mechanical properties of diatomite and silica compound-filled FKM nanocomposites is shown in figure 4. The mechanical properties of the compound filler-filled FKM nanocomposites improve first and then decline with the addition of the three coupling agents, and the mechanical properties of the nanocomposites treated with KH550 were best when the same amount of the coupling agent was introduced, in which the optimum amount of KH550 was 2 phr. It can be understood that the group of the KH550, KH590 or Si69 silanized with compound filler was all –OH group by coupling agent hydrolysed. The smallest steric hindrance among the three is observed for KH550, KH550 and the filler

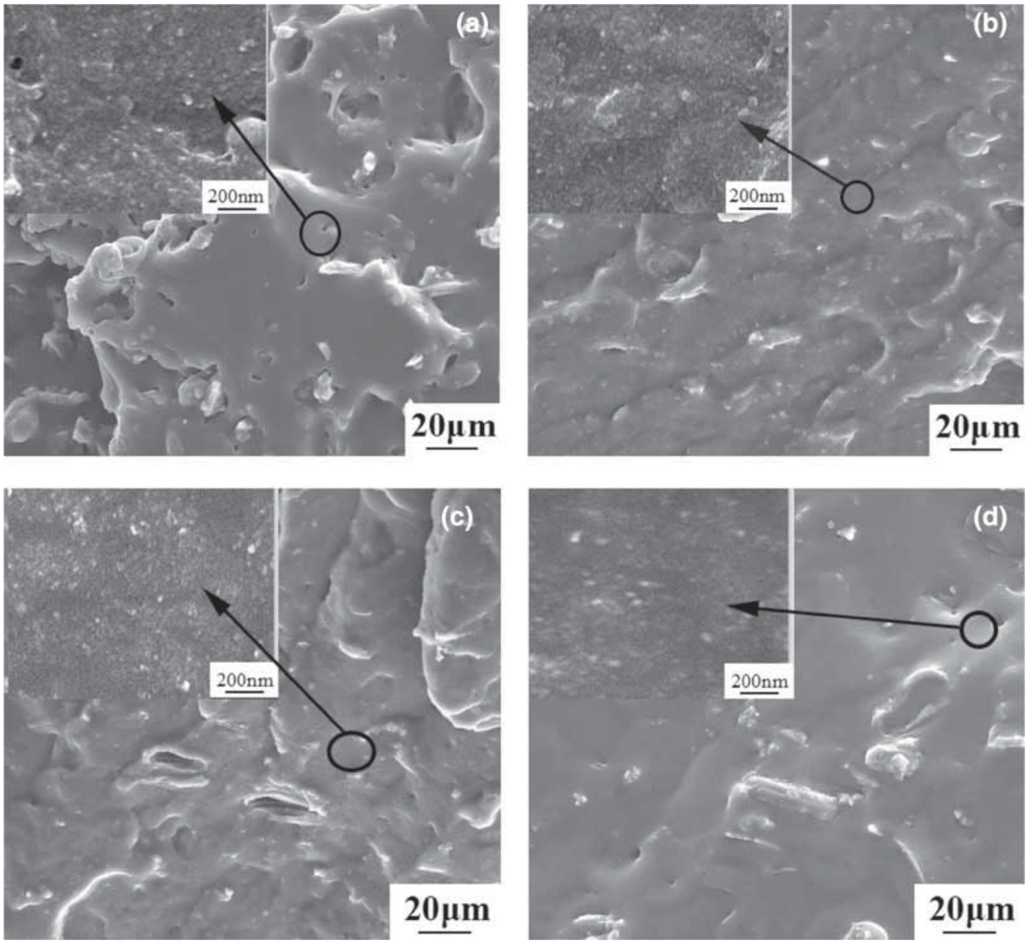

Figure 5. SEM photographs of silica and diatomite compound filler-modified FKM nanocomposites treated with the coupling agent (diatomite/silica = 8/12). (**a**) Untreated compound filler-modified FKM nanocomposites; compound filler-modified FKM nanocomposites treated with (**b**) KH590; (**c**) Si69 and (**d**) KH550.

silanize most easily, and the NH_2 group in KH550 silanizes easily with FKM, making KH550 the best coupling agent.

3.4 *SEM analysis*

SEM micrographs of untreated and treated fillers are shown in figure 5. It can be seen that the distribution of the compound filler in the fluorine rubber is obviously uneven (figure 5a) and the silica and diatomite were incompletely mixed with fluorine rubber, resulting in some layers and holes and the roughness of the sample surface was significant. The distribution of the compound filler in fluorine rubber was more homogeneous (figure 5b), and the layer and holes were fewer when KH590 was used as the coupling agent. The roughness of the sample surface was small (figure 5c) and there were some layers and holes. However, the distribution of the compound filler in fluorine rubber was more homogeneous with the coupling agent KH550 (figure 5d), suggesting that the compatibility of the compound filler and fluorine rubber was the best, providing further evidence of the results obtained on the mechanical properties.

3.5 *FTIR analysis*

As expected, the –OH peak (at 3330–3450 cm^{-1} and at 1620–1640 cm^{-1}) was associated with the stretching vibrations of the diatomite and silica surface and the $-CH_2$ peak (at 2900 cm^{-1}) was associated with the stretching vibrations of the fluorine rubber surface and the surface silanol groups (i.e., Si–OH stretching in the range of 850–980 cm^{-1}, Si–O–H and/or H–O–H bending at 1620–1640 cm^{-1} and O–H stretching of isolated silanols and hydrogen-bonded silanols at 3745 and 3740 cm^{-1}, respectively), and these are shown in figure 6. Compared with other curves, the new –NH absorption peak of the curve with KH550 appeared at 1600 cm^{-1}, suggesting that KH550 silanized with fluorine rubber generated –NH groups and the coupling agent KH550 played a role in the coupling of the filler and fluorine rubber.

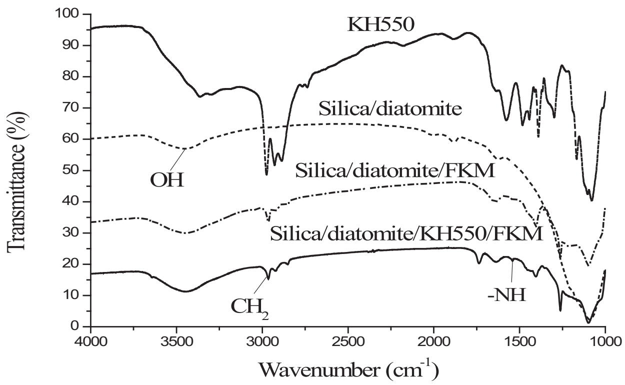

Figure 6. Infrared spectroscopy of compound filler-modified FKM nanocomposites.

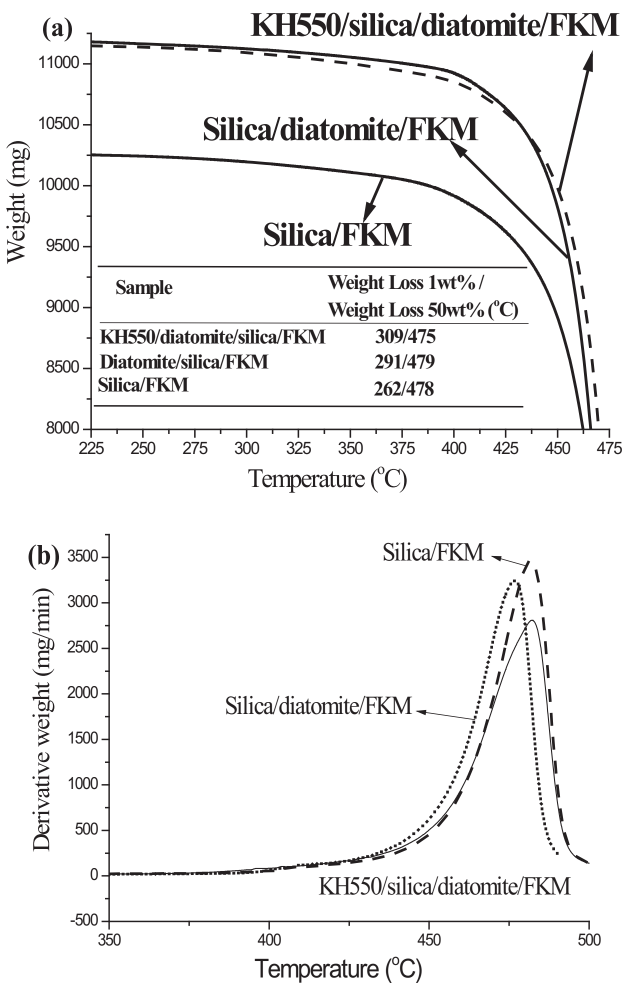

Figure 7. (**a**) TG and (**b**) differential thermogravimetry of compound filler-modified FKM nanocomposites.

3.6 *TG analysis*

As shown in figure 7, the diatomite and silica compound were used as the fillers, the temperature of heat weight loss was from 400 to 430°C, the temperatures of 1 and 50 wt% weight loss for KH550/diatomite/silica/FKM composites were significantly elevated; and its thermal stability obtained is better. The high-temperature resistance and the thermal stability of the diatomite/silica/fluorine rubber treated with KH550 make it the best among the filler systems. It can be seen that with the addition of diatomite and silica, the porous diatomite first absorbed heat when the temperature increased; then the silica absorbed heat and the fluorine rubber was heated slowly and steadily at the same time. The nanocomposites provided thermal stability, and it also provided evidence of the experimental results on the mechanical properties. Therefore, it can be concluded that the filler compound system improved the mechanical properties and thermal properties of fluorine rubber.

4. Conclusions

By comparing the effects of carbon black, silica and/or diatomite filler system on the mechanical properties of fluorine rubber, we determined that the most suitable filler system for fluorine rubber was the diatomite and silica compound, with the diatomite/silica ratio being 8:12. The best coupling agent was 2 phr of KH550. The modified compound filler treated with KH550 was silanized with fluorine rubber, thereby improving the compatibility between the fillers and fluorine rubber and further confirming the improvement in the thermal properties of fluorine rubber nanocomposites with a filler compound system.

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