

NOTE

Infrared Analysis of Effect of Recovered Clay on Natural Rubber Vulcanizates

INTRODUCTION

As a decolorant, clay is widely used in the lubricating oil industry. However, after it is used for bleaching lubricating oils, the recovered clay is often burned as an auxiliary fuel material; occasionally, the lubricating oils remained in it are extracted. Unlike filler silica and its related coupling agents which have been extensively and profoundly studied in recent years,^{1,2} the recovered clay almost has received little attention to determine whether it can be used as a filler. In this regard, the authors tried to use it as a filler for rubber.

The Fourier transform infrared (FT-IR) method has been used to study the structure of cured black-reinforced styrene butadiene rubber (SBR),³ *cis/trans*-isomerization in cured black-reinforced high *cis*-1,4-polybutadiene.⁴ In this article the FT-IR method will be used to detect the effect of the recovered clay on the network structure of natural rubber (NR) vulcanizates.

EXPERIMENTAL

The recipes of natural rubber filled with various amounts of recovered clay for structure–property tests are listed in Table 1.

The sampling technique used for FT-IR analysis was that NR vulcanizate cut from the surface of the groove of the specimen after fatigue test with a De Mattia crack testing machine at a frequency of 5 Hz was mixed with a suitable amount of KBr, then ground into powder and pressed into a KBr disc. The transmission spectra of NR vulcanizates were obtained by an FT-IR spectrometer, Model Nicolit FT-sx 170. Instrument conditions were 100 scans, 4.2 min scanning time, and 4 cm^{-1} resolutions. The size of the powder was not more than 2 μm .

RESULTS AND DISCUSSION

FT-IR Spectra of Recovered Clay-Filled NR Vulcanizates

The FT-IR spectra of NR vulcanizates filled with recovered clay and after fatigue test are illustrated in Figure

1(a) and (b). In order to identify the characteristic absorption bands of the vulcanizates, we obtained the FT-IR spectra of clay-free NR stock, its vulcanizate, and clay B as shown in Figure 2(a) and (b) and 3, respectively. From Figure 2(a), it is suggested that major absorptions of clay-free NR stock are CH_2 scissoring vibration at 1449 cm^{-1} , CH_3 at 1376 cm^{-1} , and hydrogen out-of-plane deformation in the *cis*-R'R''C=CHR system at 836 cm^{-1} , which produces a good fit to the results presented by Hummel and Scholl.⁵ However, new absorption bands appear in the spectrum of the NR vulcanizate from 699 to 611 cm^{-1} and 480 to 453 cm^{-1} at 523 cm^{-1} [Fig. 2(b)] which do not agree with polyisoprene in frequency. According to Hummel and Scholl,⁵ these new bands from 699 to 611 cm^{-1} are in the R—S—R frequency region, therefore they should be responsible for C—S stretching vibrations of monosulfidic linkages, and those at 523 cm^{-1} , from 480 to 453 cm^{-1} , are in the R—S—S—R frequency region and responsible for C—S,S—S stretching vibrations of polysulfidic linkages. Moreover, CH_2 vibration at 1449 cm^{-1} shifts to 1440 cm^{-1} , and the intensity of bands at 1376 cm^{-1} , 836 cm^{-1} becomes very weak during vulcanization of the rubber because of the C=C reaction.

Figure 3 shows that there exist quite intense absorption bands at ca. 900, 1030, and 1150 cm^{-1} , and medium strong bands at 500 and 450 cm^{-1} in the spectrum of clay B; all these bands become overlapped and broad due to SiO_2 impurity.

Based on the information discussed above, it can be shown from Figure 1(a) and (b) that the absorptions at ca. 1447, 1376, 835, and 650 cm^{-1} should be assigned to CH_2 , CH_3 , =CH, and C—S of NR vulcanizates, respectively, those at 1161 and 1041 cm^{-1} to clay absorptions, and at ca. 522 and 466 cm^{-1} to clay and polysulfidic linkages absorptions. Furthermore, a new band appears in the IR spectra of the vulcanizates at ca. 1400 cm^{-1} , which is produced by CH_2 scissoring vibration of R—S—S— CH_2 —R', R—S— CH_2 —R'.⁷

Figures 4 and 5 illustrate the peak intensities of characteristic absorption bands of the vulcanizates filled with recovered clay and after total failure.

Effect of Recovered Clay on the Structure of NR Vulcanizates

Figures 4(a) and (b) and 5(a) and (b) show the considerable increase of the absorption of clays A and B with their

Table I Recipes of Natural Rubber Filled with Recovered Clay

Natural rubber	100	100	100	100	100	100	100	100
Carbon black N330	50	40	40	40	40	40	40	40
Sulfur	2.5	2	2	2	2	2	2	2
Zinc oxide	—	3	3	3	3	3	3	3
Steric acid	—	1	1	1	1	1	1	1
Accelerator DM ^a	—	1	1	1	1	1	1	1
Accelerator CZ ^b	0.6	—	—	—	—	—	—	—
Antioxidant D ^c	—	1	1	1	1	1	1	1
Clay A ^d	—	10	20	35	—	—	—	—
Clay B ^d	—	—	—	—	10	20	35	50

^a Bis(benzothiazolyl) disulfide.

^b *N*-Cyclohexyl-2-benzothiazolyl sulfenamide.

^c Phenyl- β -naphthylamine.

^d After clay is used for bleaching lubricating oils, the recovered clay will be called clay A if the lubricating oils remaining in it are not extracted; if extracted, clay B.

contents in the vulcanizates. From this result, it is suggested that clays A and B are primarily inactive fillers and are unable to react with natural rubber to form effective clay-polymer bonds.

From Figures 2(a) and (b), 4(c) to (e) it can be shown that the concentrations of CH₂, CH₃, and =CH in NR vulcanizates increase slowly with the amount of increasing clay A, that is to say, the concentration of unvulcanized natural rubber becomes rich as the amount of clay A increases in the vulcanizates. This result means that clay A can resist an NR crosslinking reaction

to form a network structure during vulcanization of the rubber; the reason is that the intensities of absorptions of CH₂, CH₃, and =CH should weaken as the amount of the clay rises if clay A acts only as a diluent. Furthermore, Figure 4(f) and (g) demonstrates that the content of R-S-R and R-S-S-R reduces gradually when the content of clay A increases, indicating that the crosslinking density of the vulcanizates decreases while the amount of clay A increases, which is in accordance with the above discussion.

It can be seen from Figure 5(c) and (d) together with

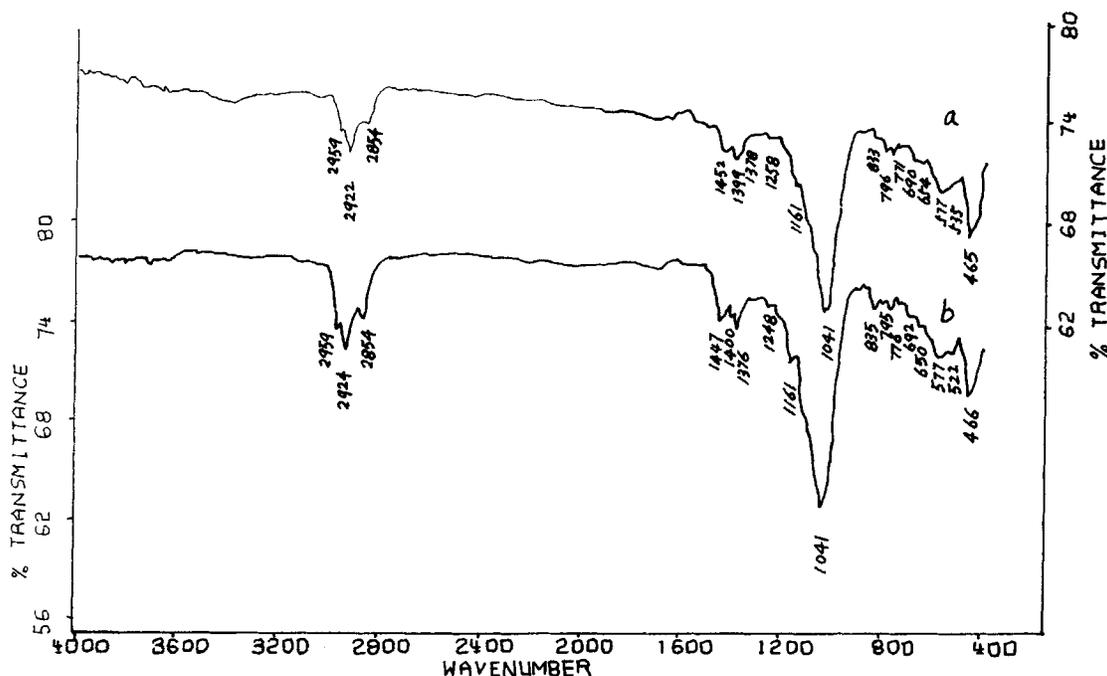


Figure 1 FT-IR spectra of NR vulcanizates filled with recovered clay: (a) clay B 50 phr; (b) clay A 35 phr

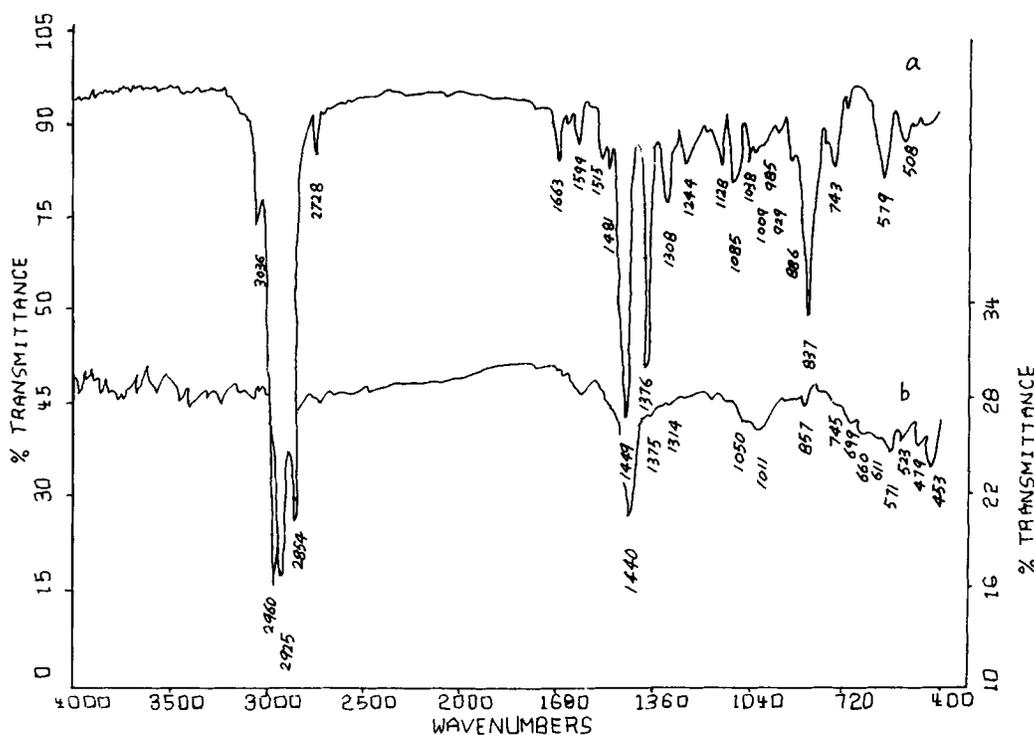


Figure 2 FT-IR spectra of NR-based compounds with NR 100 phr, carbon black N330 50 phr, sulfur 2.5 phr, and accelerator CZ 0.6 phr (a) before cure and (b) after cure.

Figure 2(a) and (b) that unlike clay A, when the amount of clay B increases, the concentration of CH_2 and CH_3 of NR vulcanizates decreases slowly and that of $=\text{CH}$ is so thin that it is almost undetectable, which infers that the content of unvulcanized natural rubber decreases slowly, and that compared with clay A both clay A and B behave as a diluent, but clay B at least does not seriously retard vulcanization of natural rubber to form a network structure, therefore bringing the concentration of unvulcanized

NR components to a lower level. Accordingly, the intensity of the absorption bands of $\text{R}-\text{S}-\text{R}$ and $\text{R}-\text{S}-\text{S}-\text{R}$ crosslinkages becomes weak as the content of clay B increases [Fig. 5(e) and (f)].

CONCLUSIONS

After being used for bleaching lubricating oils, the recovered clay acts as an inactive filler in NR vulcanizates re-

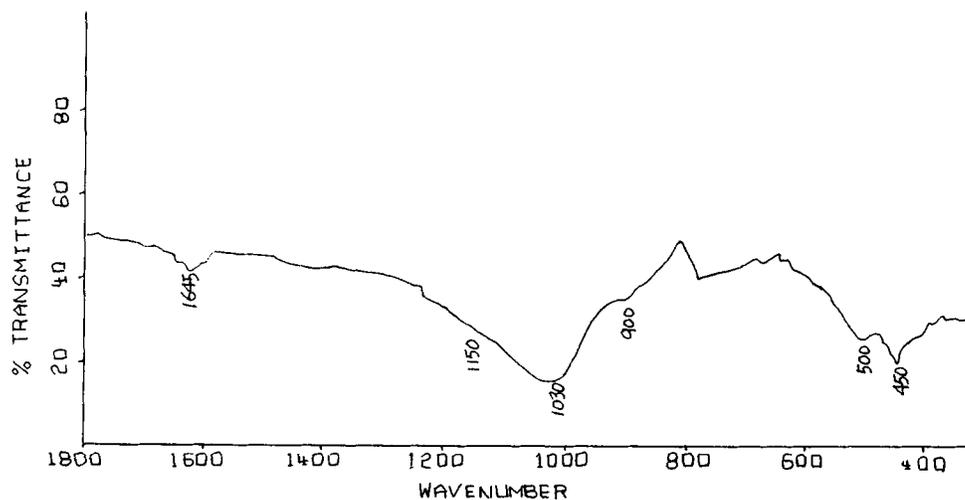


Figure 3 FT-IR spectrum of recovered clay (clay B).

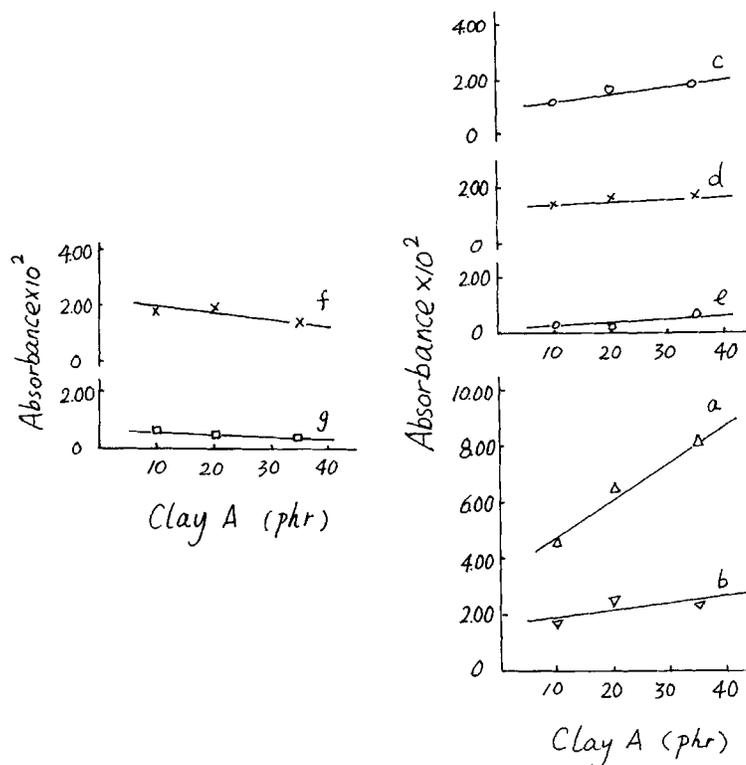


Figure 4 Effect of the content of clay A on the absorption of various structures in NR vulcanizates: (a,b) absorption of functional groups of clay A at ca. 1041 and 1161 cm^{-1} , respectively; (c,d,e) CH_2 , CH_3 , and $=\text{CH}$ at ca. 1447, 1376, and 835 cm^{-1} , respectively; (f,g) $-\text{S}-\text{S}-\text{CH}_2-$ + $-\text{S}-\text{CH}_2-$ and $\text{C}-\text{S}$ at ca. 1401 and 650 cm^{-1} , respectively.

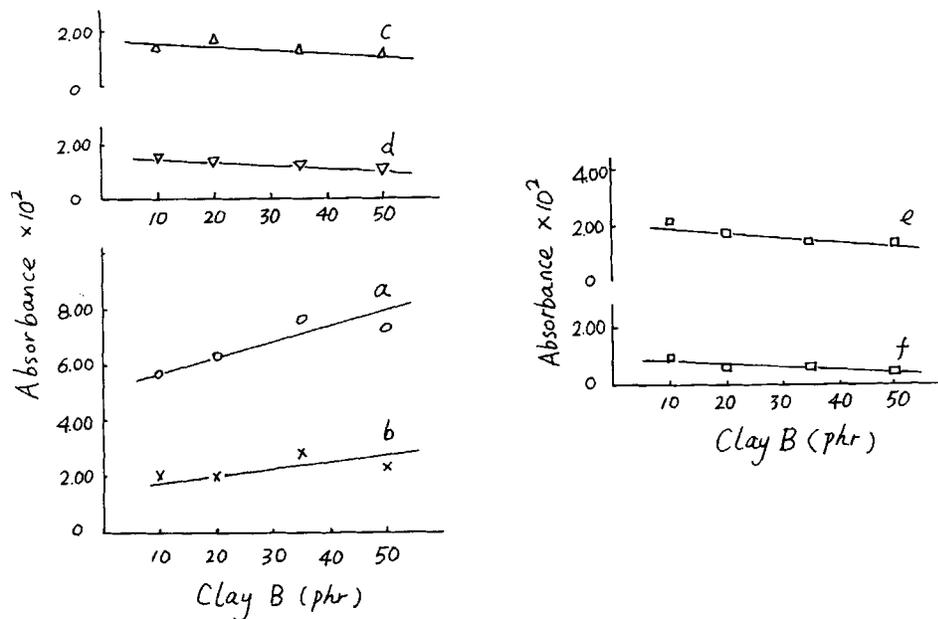


Figure 5 Effect of the content of clay B on the absorption of various structures in NR vulcanizates: (a,b) absorption of functional groups of clay B at ca. 1041 and 1161 cm^{-1} , respectively; (c,d) CH_2 and CH_3 at ca. 1452 and 1378 cm^{-1} , respectively; (e,f) $-\text{S}-\text{S}-\text{CH}_2-$ + $-\text{S}-\text{CH}_2-$ and $\text{C}-\text{S}$ at ca. 1399 and 654 cm^{-1} , respectively.

ardless of whether the lubricating oils remained in it have been extracted (clay B) or not (clay A). The filler could not react with natural rubber to form effective clay-polymer bonds in the vulcanizates. Accordingly, the mono-sulfidic, polysulfidic linkages of the vulcanizates decrease.

Compared with clay B, clay A can retard the formation of crosslinkages in NR vulcanizates.

REFERENCES

1. S. Wolff, (1982) *Rubber Chem. Technol.*, **55**(4), 967.
2. M-J Wang, S. Wolff, & J. B. Donnet, (1991) *Rubber Chem. Technol.*, **64**(5), 714.
3. E. F. Devlin, (1981) *J. Polym. Sci., Lett. Ed.*, **19**, 189.
4. E. F. Devlin, and A. L. Mengel, (1984) *J. Polym. Sci., Polym. Chem. Ed.*, **22**(3), 843
5. D. O. Hummel, and F. Scholl, (1988) *Atlas of Polymer and Plastics Analysis*, Vol. 2, Part b/I, Carl Hanser

Verlag, VCH Verlagsgesellschaft, Berlin, pp. 342, 309, 269.

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