NOTES

Effect of Natural Aging on the Dielectric Properties of Natural Rubber Mixed with Some White Fillers

INTRODUCTION

Weathering has a destructive effect on rubber known as aging. The most important factors in aging are oxygen and ozone.[1,2] The aging of rubber products is the net result of chemical reactions and changes of a physicochemical nature. The durability of rubber makes the testing of its resistance to oxidation difficult because of the time element. The dielectric properties of samples of natural rubber mixed with channel black aged for nine years[3] and synthetic rubber samples aged for approximately five years[4] were studied previously. The aim of this communication is to extend this study to samples of natural rubber mixed with silica, domestic calcium carbonate, or precipitated calcium carbonate subjected to natural aging for approximately six years.

EXPERIMENTAL

The dielectric constant ϵ' and dielectric loss ϵ'' were measured for aged samples of natural rubber mixed with 0%, 10%, 30%, and 60% by weight silica and 0%, 30%, 100%, 200%, and 300% by weight domestic $CaCO_3$ or precipitated $CaCO_3$. The samples were subjected to natural aging for approximately six years.

The measurements were carried out in the frequency range from 60 Hz to 10 MHz with the same equipment used previously. Up to 300 kHz, a Schering bridge from Rohde & Schwarz was used. A multidecameter (DK06) from WTW based on the superhetrodyne principle was utilized for frequencies between 10^5 and 10^7 Hz. Guard ring capacitors were used with both decameters, and the accuracy of the measurements equals 1% in ϵ' and 2% in ϵ''.

RESULTS AND DISCUSSION

Natural Rubber Mixed with Silica (SiO_2)

Figures 1 and 2 show the results of ϵ' and ϵ'' obtained for the aged samples. Comparing these results with those for the same unaged samples,[5] it is clear that the values of ϵ' for all samples are decreased

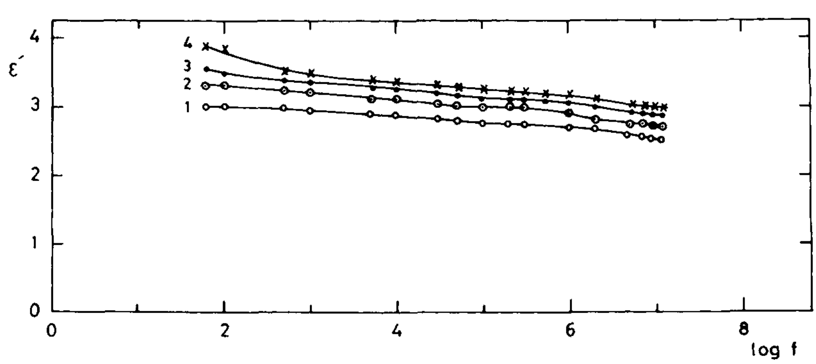


Fig. 1. Dielectric constant ϵ' vs. log f for natural rubber samples loaded with: (O) 0%; (⊙) 10%; (●) 30%; (X) 60% silica (parts silica per hundred parts rubber).

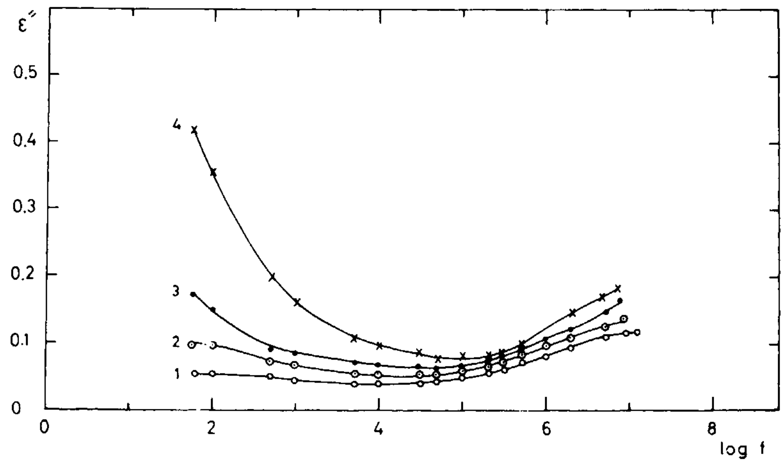


Fig. 2. Dielectric loss ϵ'' vs. log f for natural rubber samples. Same notation as in Fig. 1.

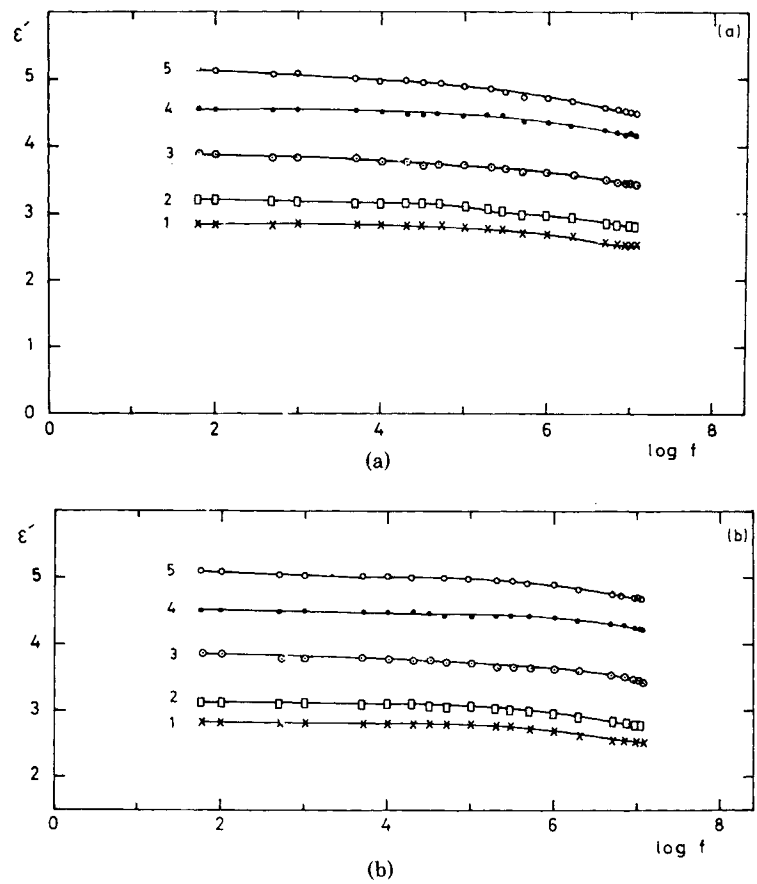
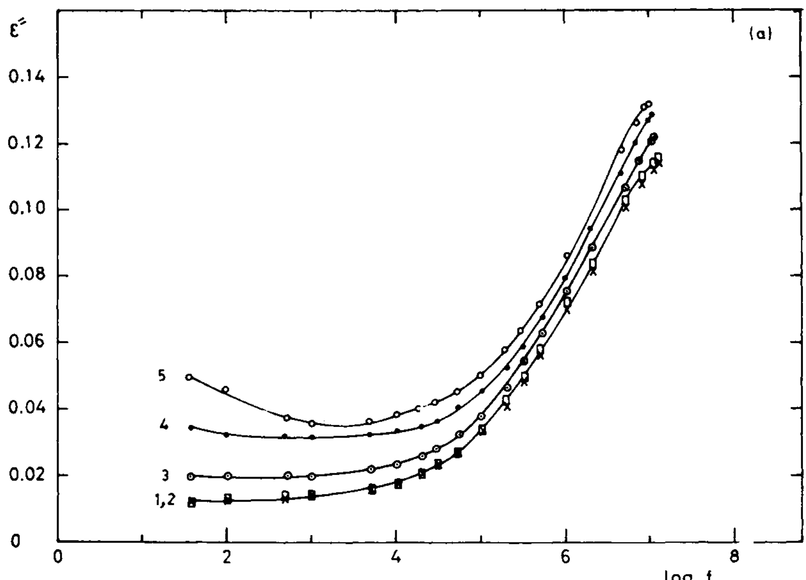
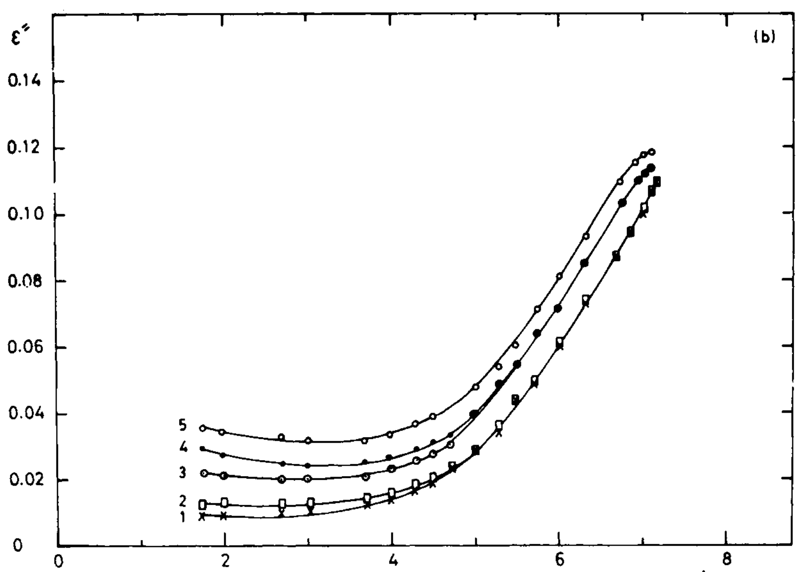


Fig. 3. Dielectric constant ϵ' vs. log f for natural rubber mixed with (a) domestic calcium carbonate and (b) precipitated calcium carbonate. The $CaCO_3$ concentrations used are: (×) 0%: (□) 30%; (⊙) 100%; (●) 200%; (○) 300%.



(a)



(b)

Fig. 4. Dielectric loss ϵ'' vs. $\log f$ for natural rubber mixed with (a) domestic $CaCO_3$ and (b) precipitated $CaCO_3$. Same notations as in Fig. 3.

especially in the low frequency region up to 10^5 Hz. The change in ϵ' is minimal for higher frequencies.

Looking at the ϵ''-graph, there appears to be a loss peak at 10^7 Hz which may be a characteristic of the polymer with some effect due to the filler. This loss peak is slightly decreased by aging and its position seems not to be changed. There appears to be also a second peak below 10^2 Hz, which might be related to the filler. This peak seems to either become smaller or shift to lower frequencies with aging.

As SiO_2 is a reinforcing agent, so in the unaged rubber samples, it is suggested that strong interaction with silica occurs and is responsible for the rapid increase in ϵ' and ϵ'' with an increase in silica content. For the aged samples, oxidation may reduce this strong interaction resulting in a pronounced decrease in ϵ' and ϵ'' in the low-frequency region. For the silica free sample, ϵ'' is increased in the low-frequency region. These results show that the electrical properties of the vulcanizate containing silica do not become weaker on aging.

Natural Rubber Mixed with Calcium Carbonate ($CaCO_3$)

The results of the dielectric constant ϵ' obtained for rubber samples mixed with domestic $CaCO_3$ and precipitated $CaCO_3$ are given in Figure 3a and b, respectively. Comparing these results with those for the same unaged samples,[5] it is found that in the case of precipitated $CaCO_3$ samples, the dielectric constant ϵ' had not changed while those samples mixed with domestic $CaCO_3$ had increased only by about 3%. These are within normal variations.

On the other hand, the dielectric loss ϵ'' had increased for both types of $CaCO_3$ samples as seen from Figure 4a and b compared with the corresponding results for the unaged samples,[5] especially in the high-frequency region. The position of the strong loss peak appearing at 10^7 Hz for the unaged samples seems to be shifted slightly toward higher frequencies on aging. The increase in ϵ'' may be due either to a slow process going on in the sample between the rubber and the inert filler ($CaCO_3$) or to the migration of ingredients. The absorption of moisture is not favored, since the increase in ϵ'' would then be more noticeable in the low-frequency region than in the high-frequency region, which is not the case.

References

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Received July 2, 1976
Revised August 20, 1976