

Environmental Effects and Relaxation in Natural Rubber

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Synopsis

The change in attenuation of longitudinal ultrasonic waves has been measured as a function of frequency and temperature for natural rubber samples loaded with intermediate super abrasion furnace (ISAF) in increasing quantities and vulcanized with *N*-oxidiethylene benzotriazol sulfunamid (OBTS) after being subjected to natural aging for 5 years. Three relaxation processes, namely α , β , and γ , were noticed. The activation energy for each process was calculated and the results are discussed. Also, the dielectric constant ϵ' and dielectric loss ϵ'' have been investigated for those samples after being immersed in various water media. The measurements were carried out in the frequency range from 100 Hz up to 100 kHz and at room temperature ($\sim 28^\circ\text{C}$). The results are compared with each other and the differences are interpreted.

INTRODUCTION

The dielectric properties of natural rubber samples mixed with furnace^{1,2} and channel³ black were studied. The effect of natural aging on the dielectric properties of such samples was also studied.⁴⁻⁶ The aim of this work is to extend this study and investigate the effect of various water media on the dielectric properties of these samples, and also to study the relaxation processes of such samples using the ultrasonic technique.

EXPERIMENTAL

The dielectric constant ϵ' and dielectric loss ϵ'' were measured for the age samples of natural rubber loaded with intermediate super abrasion furnace (ISAF) in increasing quantities and vulcanized with *N*-oxidiethylene benzotriazol sulphunamid (OBTS).

The formulations of these samples are given in Table I. These samples were immersed in various water media; tap water, Nile water, swimming pool water, and Mediterranean Sea water. ϵ' and ϵ'' were measured daily until they reach saturation. To reach saturation, the samples should be immersed for 2 weeks at least. After making sure of saturation, ϵ' and ϵ'' were measured immediately after taking off from water and at successive intervals till the values of ϵ' and ϵ'' become mostly stable.

ϵ' and ϵ'' were measured using an NF, a Schering bridge-type decimeter, in the frequency range between 100 Hz and 100 kHz. A guard ring capacitor type NFM/5T was used. Accuracy of measurements in ϵ' was $\pm 1\%$ while for ϵ'' it was $\pm 2\%$. A description of the instrument and method used for measure-

TABLE I
Formulations of Natural Rubber Mixture Samples

Ingredient	phr ^a
Standard Malaysian rubber	100
Zinc oxide	5
Stearic acid	1.5
OBTS	0.5
Sulfur	3
ISAF	0, 10, 20

^a phr = per hundred parts rubber.

ments and calculations are given in the instruction sheet by Wiss. Techn. Werkstten Weilheim Obb., West Germany (WTW). The samples were in the form of discs 55 mm diameter and 4 mm thickness. Measurements were carried out at room temperature ($\sim 28^\circ\text{C}$).

The ultrasonic absorption through the aged samples was measured using a conventional pulse-echo technique.⁷ An ultrasonic flaw detector USM2 produced by Krautkramer was used. The apparatus is capable of producing high frequency pulses in the frequency range 0.5–12 MHz and usually operates with the same transducer as transmitter and receiver at the same time. Since the ultrasonic absorption α in polymers is much higher than that in metals, usually only one or two echoes are observed in the oscilloscope. Accordingly, measurements were taken on a comparative basis where the variation of l^{-1} (l is the height of a particular echo on the oscilloscope) with temperature is considered to represent the variation of α with temperature, since they are related to each other by the equation, $l = l_0 e^{-\alpha d}$ and have the same dimensions.^{8,9} d is the distance traversed and l_0 is the amplitude of the pulse at $d = 0$. The measurement of the height of a particular echo l , on the face of the oscilloscope, was made by means of calibrated scale capable of measuring with an accuracy of ± 0.2 mm. The ultrasonic measurements were carried in the frequency range between 2 and 5.7 MHz and at temperatures between 170 and 353 K. The temperature was achieved using an electric furnace.

RESULTS AND DISCUSSION

The change in attenuation of the longitudinal ultrasonic waves with temperature for the samples containing 0, 10, and 20 phr filler after being subjected to natural aging for 5 years is represented in Figures 1(a), (b) and (c), respectively. Series of peaks are obtained whose positions on the temperature scale shift to higher temperatures with increasing frequency. These peaks are considered to be α , β , and γ relaxations, respectively. α -Relaxation may be attributed to the large scale conformational rearrangements of the main chain¹⁰ while β -relaxation can be attributed to the orientation of the polar groups. The third process which is considered to be the γ -relaxation is attributed to the dipolar sulfur groups. Such a region is similar to that found before in the case of natural rubber samples loaded with channel or furnace black and containing relatively high amounts of sulfur,^{3,1} which may react with carbon to form carbon-sulfur complexes.³

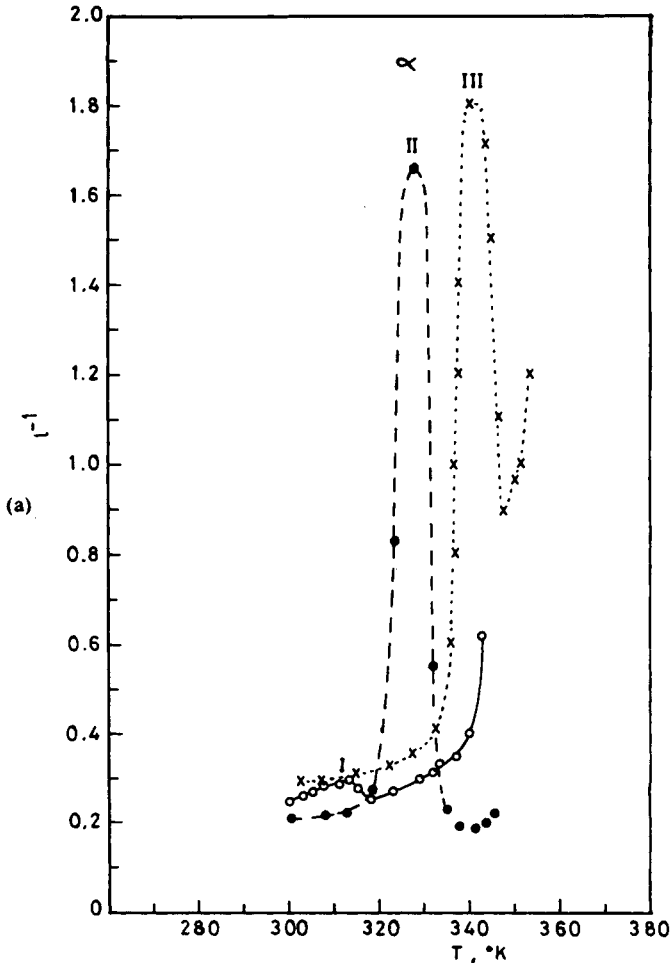


Fig. 1. Relation between l^{-1} (cm) and T (K) at frequencies (I) 2 MHz, (II) 3.14 MHz, and (III) 5.7 MHz for natural rubber loaded with (a) 0 phr filler, (b) 10 phr filler and (c) 20 phr filler.

From Figure 1 it is also found that the peaks which characterize the different relaxation processes shift to lower temperatures by increasing the carbon content in the sample.

To calculate the apparent activation energy E for each process, $\log f$ is plotted graphically against $1/T_m$ (the reciprocal of the absolute temperature at which the peak occur). A straight line is obtained in each case. From the slope of these straight lines and by using Arrhenius equation,¹¹ the activation energies are obtained and given in Table II.

These values are comparable with those found in the literature¹² for such processes. From this table it is also noticed that the activation energy for each process increases with the increase in carbon content, which may be due to the increase in hardness with the increase in carbon content.

Figure 2 shows the variation of the dielectric constant ϵ' and dielectric loss ϵ'' with time (time starts when the samples are taken off immediately from the various water media). ϵ' and ϵ'' are found to decrease by increasing time

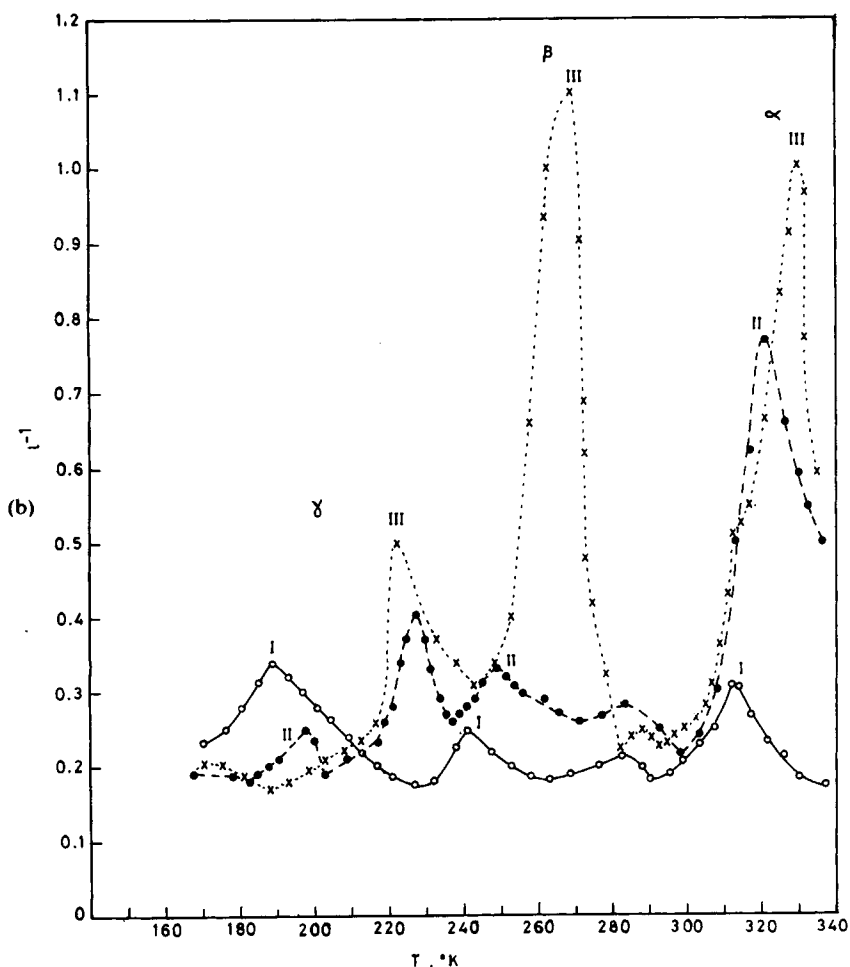


Fig. 1. (Continued from the previous page.)

until no detectable change is obtained. This happened when most of the absorbed water is evaporated from the samples. The moisture is found to be more pronounced in case of pure gum while its effect diminishes by increasing the percentage of ISAF filler in the sample. This is attributed to the ability of the sample to absorb water from the environmental water media which is found to be inversely proportional to the hardness of the sample.

Figure 3 illustrates the variation of ϵ' and ϵ'' with frequency after 5 h of taking the samples off from water. At that time ϵ' and ϵ'' become mostly stable. ϵ'' for the samples immersed in the various water media are higher than those for unimmersed ones.⁶ This is attributed to the higher value of dielectric constant of water (78.54).¹¹ On the other hand, ϵ' is found to decrease by increasing frequency while a peak is noticed in the absorption curve relating ϵ'' and $\log f$. This peak may be attributed to the formation of bigger aggregates. For pure gum, it is found that the rate of decrease of ϵ' with frequency is higher. The observed peak in the absorption curve is sharper. By increasing the filler content in the sample, the variation of ϵ' with

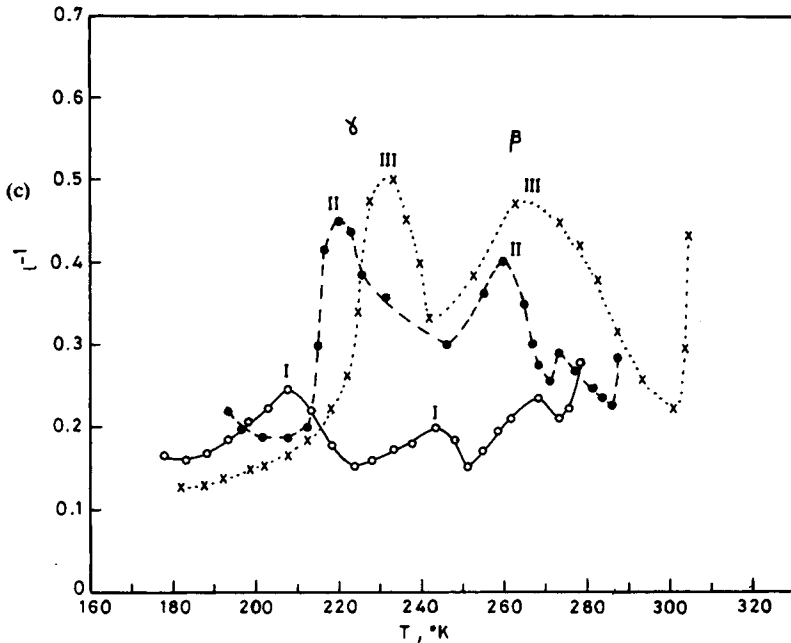


Fig. 1. (Continued from page 2441.)

frequency decreases while the ϵ'' peak becomes broader. This is attributed to the decrease in absorbed water by increasing the filler content in the sample as mentioned before. From Figure 3 it is also found that ϵ' and ϵ'' in the cases of swimming pool water and Mediterranean Sea water are higher than those for tap water and Nile water. This could be attributed to the presence of chlorine in swimming pool water and sodium chloride in Mediterranean Sea water.

So, it could be concluded that three relaxation processes were noticed in natural rubber samples loaded with intermediate super abrasion furnace (ISAF) and vulcanized with *N*-oxidiethylene benztriazol sulfunamid (OBTS). These relaxations are attributed to main chain, polar groups and to the dipolar sulfur groups present in the samples. Also, it is concluded that the presence of those samples in various water media does not affect much their dielectric properties. That makes such samples to be more preferably used as insulators when immersed in various water media especially the samples containing 20 phr ISAF filler.

TABLE II
The Activation Energy E for Different Processes in Samples
Having Different Concentrations of Carbon Black

Carbon content (phr)	E (kcal/mol)		
	α	β	γ
0	8.3	—	—
10	11.9	5.0	2.6
20	—	6.3	3.6

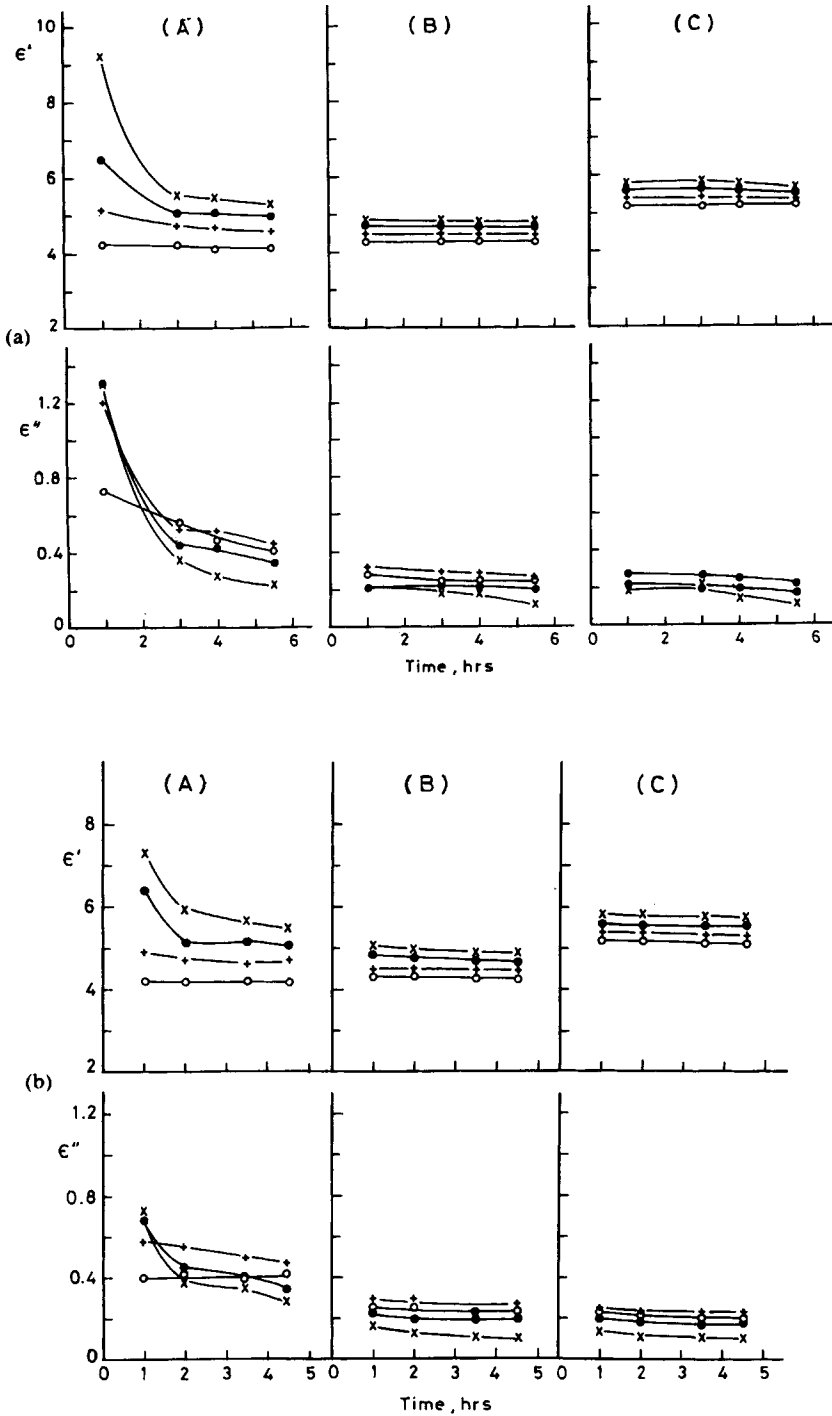


Fig. 2. Variation of ϵ' and ϵ'' with time (h) (time starts when the samples are taken off immediately from the various water media) at frequencies (\times) 100 Hz, (\bullet) 1 kHz, ($+$) 10 kHz, and (\circ) 100 kHz for natural rubber loaded with (A) 0 phr filler, (B) 10 phr filler, and (C) 20 phr filler, immersed in (a) tap water, (b) Nile water, (c) swimming pool water, and (d) Mediterranean Sea water.

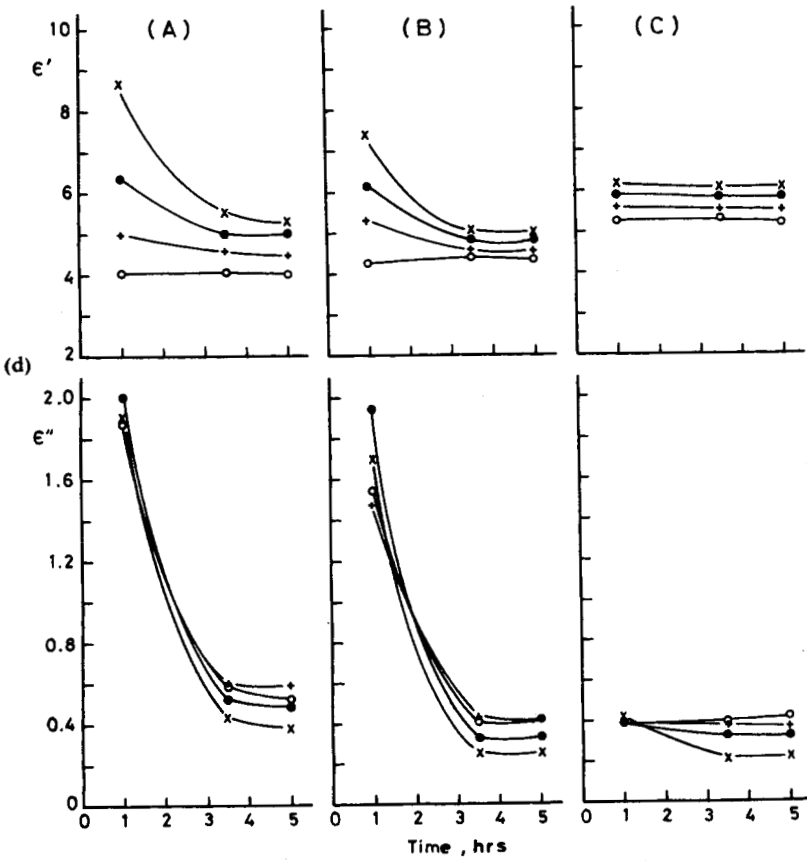
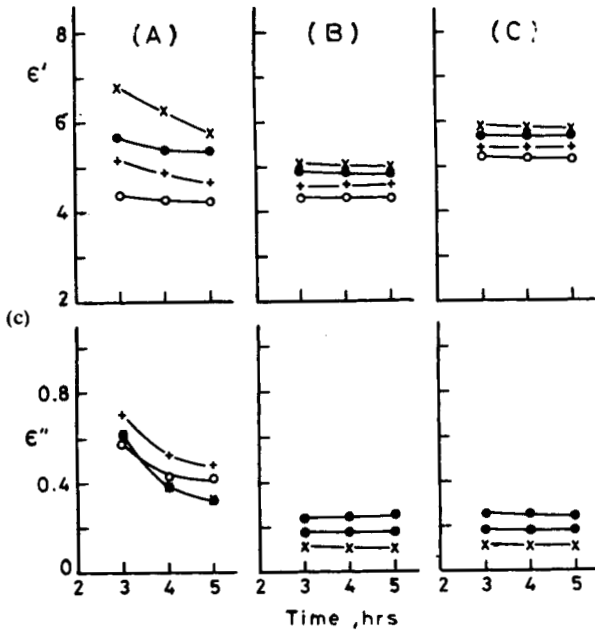


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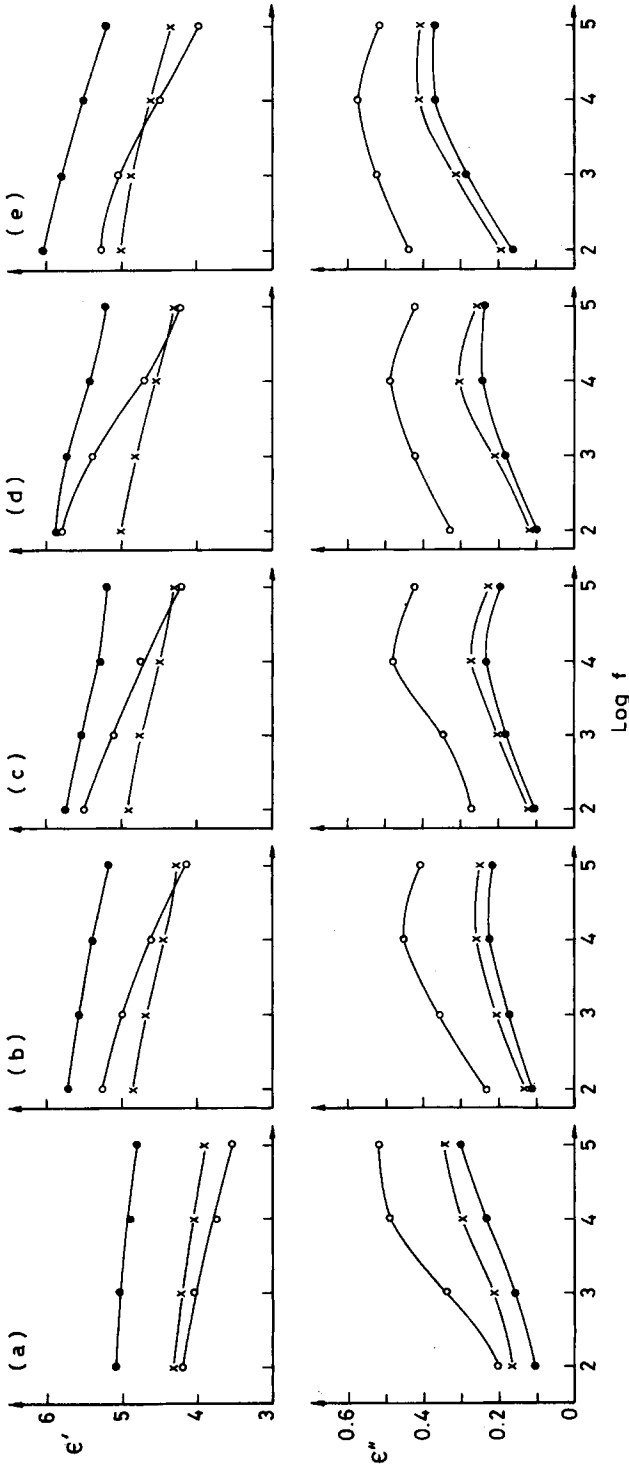


Fig. 3. Variation of ϵ' and ϵ'' with frequency for natural rubber loaded with (○) phr filler, (×) 10 phr filler and (●) 20 phr filler: (a) before immersing in different water media; (b) after immersing in tap water; (c) after immersing in Nile water; (d) after immersing in swimming pool water; (e) after immersing in Mediterranean Sea Water.

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Received June 3, 1986

Accepted September 23, 1986