

SYNTHESIS AND THERMAL -ELECTRICAL STUDIES OF SOME
MOULDED EPOXY-NOVOLAC RESINS

BY

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ABSTRACT

High temperature and electrical insulating moulded samples have been prepared from different types of epoxy: and novolac resins. The effect of epoxy-phenolic resins structure on the thermal stability and dielectric properties of these samples has been studied.

INTRODUCTION

Epoxy-novolac resins are considered the most important and widely employed synthetic resins in the field of thermal and electrical insulators. These copolymers could have better mechanical and electrical properties [1].

In this investigation, a limited programme of work has been undertaken to obtain some general indications of the effect of epoxy-phenolic resins structure on thermal and electrical properties of moulded samples filled with fiber

-Dielectrics part was done in the NRC by Dr. A.L.G. SAAD.

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glass after long term heat ageing. The thermal stability of these samples (at 180 -200°C till 250 hrs.) and their dielectric properties (before and after heating) over the frequency range from 100 Hz to 50 kHz at different temperatures from 30 to 60°C have been studied.

EXPERIMENTAL

Materials:

Phenol formaldehyde Novolac resin (N-standard), drop falling temperature 110°C, and cresilic acid product of El-Nasr Co. for coke and industrial chemicals; Egypt (its characteristics and chromatographic resolution are given in Tables 1,2).

TABLE 1
Characteristics of Cresilic Acid.

Boiling range, °C	Dry yield, %	Average molecular weight	Specific gravity	Refractive index	Viscosity at 30°C, m.ps.	Elemental analysis, %		
						C	H	N
175-210	96	120	1.046	1.5458	8.225	85.62	8.41	-

TABLE 2
Chromatographic Resolution of Cresilic Acid⁽²⁾.

Phenol, %	Cresol, %			Xylenols, %
	o-	p-	m-	
0.007	14.993	2.90	62.40	19.70

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Synthesis of Novolac Resin (N)

The mixture of phenol (38 gm) and formaline 40% (15 gm) was shaken until complete dissolution and then hydrochloric acid $d=1.19$ (0.5 gm) was added. The mixture was heated at 90–100°C for 20–40 min. and the experiment was conducted according to the method previously [3] described (its drop falling temperature 112–115°C).

Synthesis of Bisphenols (B)

Pure phenol (75 ml), o-cresol (86.4ml) or cresilic acid (80 ml) were mixed with acetone (15 ml) and dry toluene (200 ml) in presence of dry hydrogen chloride gas according to the procedure described in the literature [2,4]. The characteristics of obtained bisphenols BA, BO and BC, respectively are given in Table 3.

TABLE 3
Characteristics of Prepared Bisphenols

Type	Yield, %	Melting point, °C	Average molecular weight	Elemental analysis, %		
				C	H	N
BA	80	155	230	72	7.1	-
BO	90	130	243	79	8.0	-
BC	85	99	253	78	7.7	-

EA = bis(4-hydroxyphenyl) propane

BO = bis(4-hydroxy-3-methylphenyl) propane

EC = mixture of BA, BO ,

bis(4-hydroxy-2-methylphenyl) propane and

bis(5-hydroxy-2-methylphenyl) propane .

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Synthesis of Low Molecular Weight Epoxy Resins (E)

Bisphenols BA, BO or BC (228 g), epichlorohydrin (235.9 ml) and sodium hydroxide solution (2.2 mole in 100 ml H₂O) were mixed at 65-70°C and the experiment was conducted according to the method described in the literature [5,6]. The characteristics of obtained low molecular weight epoxy resins EA, EO or EC, respectively are given in Table 4.

TABLE 4
Characteristics of Prepared Epoxy Resins.

Epoxy type	Parent bisphenol	Average molecular weight	Viscosity at 50°C, m.ps	Drop falling temp, °C	Epoxy group content, %	Hydroxy group content, %	Elemental analysis, %		
							C	H	N
EA	BA	320	326.9	50	21.622	12.43	70.18	7.01	-
EO	BO	355	225.3	48	22.099	19.22	71.66	7.63	-
EC	BC	374	113.77	45	26.31	28.70	73.37	7.79	-

To improve the thermal [7] and electrical [1] properties of epoxy resins, novolac resin can be used to produce modified epoxy resins. Therefore, equal weight of prepared novolac resin N and epoxy resins EA, EO or EC were mixed to produce NEA, NEO or NEC samples, respectively.

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Preparation of Moulded Samples:

According to the method described in the literature [1], the soluble prepared resins (50%) were dissolved in the least amount of acetone and the following constituents were then added in %; calcium oxide (3.0), colophony (2.0), paraffin wax (1.0), hexamethylenetetramine (8.0) and stearic acid (1.0). These constituents were thoroughly mixed, dried at room temperature and ground to fine powder. Then, the glass fiber; diameter 7 μ and length 50 mm (35.0 %) was added. The moulding powder and glass fiber were pressed to form a disc (diam = 55 mm, thick. = 3 mm) using Paul Weber Machine-U.Apparatelov, Furhrbochsta, Be 4, D 7064 Remshalden-Grunbach under 150 kg/cm². The temperature was increased gradually till 180 -200°C. The time for hardening did not exceed 20 min. It is significant to point out that glass fiber increases the chemical stability [8] and dielectric constant [9] of the cured epoxy resin and improves mouldability [8].

The moulded samples were evaluated through their thermal stability (at 180 -200°C till 250 hrs.) and their dielectric properties.

Thermal Stability Test:

Thermal stability of the prepared moulded samples was evaluated by weighing dry samples and placing them in a muffle furnace at 180 -200°C for different periods of time till 250 hrs. The weight loss (%) after cooling to room temperature was then evaluated after each period.

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Dielectric Measurements:

The permittivity (ϵ') and power factor ($\tan \delta$) were measured in the frequency range 100 Hz - 50 k Hz using a WTW NF decameter of the Shering bridge - type [10]. A guard -ring capacitor type NFM/5T was used. The precision of the measurements of ϵ' was $\pm 1\%$ while for $\tan \delta$, it was $\pm 2\%$. Description of the instruments and methods used for measurements and calculations are given before. Measurements were carried out at temperatures between 30 and 60°C using an ultra thermostat.

Conductivity Measurements:

To measure the d.c. conductivity, the direct current power supply unit GMU 516/01 (Philips) was used. This gives a stable d.c. voltage between 0 and 200 V with a maximum permissible loading current of 1 mA. The voltage across the sample and the current flowing through it were measured using a multimeter type URI BN 1050 from Rhode and Schwarz.

RESULTS AND DISCUSSION

A- Investigated Samples:

In this study, different moulded samples have been prepared from;

1. Novolac phenol formaldehyde resin (N). For comparison, one moulded sample has been prepared from commercial novolac resin (N-standard).

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2. Different types of low molecular weight epoxy resins namely; homopolyepoxy resin EA based on bis (4-hydroxyphenyl) propane prepared from phenol, homopolyepoxy resin EO based on bis (4-hydroxy-3-methylphenyl) propane prepared from o-cresol and copolyepoxy resin EC prepared from cresilic acid which consists of phenol and o-, m-, & p- cresols based on mixture of:
 - bis (4-hydroxyphenyl) propane (from phenol).
 - bis (4-hydroxy-3-methylphenyl) propane (from o-cresol)
 - bis (4-hydroxy-2-methylphenyl) propane (from m-cresol)
 - bis (5-hydroxy-2-methylphenyl) propane (from p-cresol)
3. Equal weight of novolac resin (N-prepared) and epoxy resins EA, EO, or EC to produce NEA, NEO or NEC samples, respectively.

B- Thermal Stability of the Moulded Samples:

Thermal stability of the prepared samples has been achieved by heating them at 180 -200°C for different periods of time and evaluated in terms of weight loss (%). The obtained results are given in Table 5.

It is evident from the data presented in Table 5 that the thermal stability of epoxy resins increases on mixing them with prepared novolac phenol formaldehyde resin N where the values of weight loss (%) of NEA, NEO and NEC samples decrease in comparison with EA, EO and EC samples, respectively. It is significant to point out that novolac resin may act as

TABLE 5
Thermal Stability of the Prepared Moulded Samples
(ageing at 180 -200°C for different times(t), hours).

Sample type	t	Weight Loss, %									
		5	10	30	50	70	100	140	180	250	
N-Standard		1.221	1.846	2.254	2.659	3.060	3.680	4.010	4.050	4.110	
N		1.366	2.079	2.613	3.310	4.460	5.660	5.920	6.159	6.190	
EA		1.206	1.737	2.007	2.280	2.550	3.350	3.610	3.662	3.670	
NEA		0.690	1.067	1.186	1.377	1.1509	1.740	2.090	2.053	2.010	
EO		0.890	2.027	2.451	2.968	3.406	4.470	5.550	5.716	5.760	
NEO		1.084	1.706	2.064	2.418	3.138	3.821	4.630	4.751	4.822	
EC		1.405	1.982	2.546	3.077	3.609	4.860	5.812	6.109	6.032	
NEC		0.740	1.356	1.610	1.881	2.029	2.550	2.962	3.163	3.191	

additional curing agent for completing the curing process with formation of a highly cross-linked compound of phenolic epoxy resin having a lower weight loss (%) i.e., a higher thermal stability. These results are in agreement with the literature [9] where thermal stability of cured epoxy resin system depends in part on the chemical structure and hydrogen bonds as well as on the functionability and cross-linking density of the resin.

Results given in Tables (4 and 5) show also that the thermal stability and heat resistance for the moulded sample EA based on epoxy resin molecule free from methyl groups and having lowest hydroxy group content (12.43%) is better than the sample of EO based on epoxy resin molecule containing

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few methyl groups in ortho position and having hydroxyl group content (19.22%), and still much better than sample EC based on epoxy resin molecule containing many methyl groups in ortho, meta & para positions and having largest percent of hydroxyl group content (28.70%). This phenomenon may be attributed to the presence of methyl and hydroxyl groups which may be subjected to oxidation to an aldehyde.

C- Dielectric Properties of Moulded Samples:

I. Standard and Prepared Novolac Resins:

The results obtained for the permittivity (ϵ') and power factor ($\tan \delta$) versus frequency for standard and prepared novolac resins at different temperatures are shown in Fig. 1. It is clear that for both types of novolac resins, there is a region of absorption in the low frequency range where the maximum in the power factor is not reached at the low frequency limit of the measurement. This region is characterized by high permittivity and high power factor which may be due to the rotation of large aggregates, of the chain or moisture content. However, Fig. 1 shows only a slight decrease in the values of ϵ' and $\tan \delta$ for N-prepared resin as compared with those of the N-standard one. So, it may be concluded that standard and prepared novolac resins have almost the same dielectric properties.

II. Novolac N, Epoxy resin EA and their Mixture NEA:

The effects of changing the permittivity (ϵ') and power factor ($\tan \delta$) of these samples with frequency at the investigated temperatures are shown in Fig. 2.

It is evident from Fig. 2 that ϵ' increases by increasing the temperature and decreases by increasing the applied frequency. Similar results are obtained in the literature [1]. The increase of ϵ' with temperature can be explained by the increase in the mobility of polar groups, decrease in density and hence a decrease in the effect of the environment which facilitates the orientation of the mobile groups. The decrease of ϵ' with frequency may occur due to the dielectric dispersion. Moreover, Fig. 2 shows that the values of ϵ' for N sample are higher than those of EA sample whereas the values of ϵ' for NEA sample are observed between them. This may indicate that ϵ' for EA sample is improved by the addition of N resin.

From the absorption curves relating $\tan \delta$ and $\log f$, it has been found that for EA and NEA samples, there is a peak whose maximum lies around 1 k Hz which may be attributed to Maxwell-Wagner effect [11]. This effect may be due to an a.c. current in phase with the applied potential. This current results from the differences in the conductivities and the permittivities of the different constituents of the investigated samples. To check that these losses in that range of frequency are not due to d.c. conductivity, Ohm's law was

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applied to direct currents flowing through the samples at different voltages ranging from 0 to 200 V. No detectable current is seen to flow through the samples, indicating that they have no d.c. conductivity.

It is interesting to study the effect of higher temperatures on the dielectric properties of these samples. So, after heating the same samples at (180 -200°C) for 250 hrs., and $\tan \delta$ were measured again and the results are represented by dashed lines on Fig. 2. It is evident from these results that both ϵ' and $\tan \delta$ for all samples are largely decreased. It is significant to point out that the rate of this decrease is higher for N sample as compared with that of EA sample. This is in accordance with the literature [12] in that EA sample has a greater resistance to the dielectric degrading effect of moisture. Also, the position of the loss maximum for EA and NEA samples is not changed by heating. This indicates that the thermal heating does not show any effect on the constitution of the samples. So, the large decrease noticed in ϵ' and $\tan \delta$ could be due to the loss of the sample's moisture content by heating.

III. Novolac N, Epoxy Resin EO and Their Mixture NEO:

The dielectric properties of N, EO and NEO samples are also investigated. The results for ϵ' and $\tan \delta$ versus frequency are shown graphically in Fig. 3. Similar to that found in Fig. 2, the values of ϵ' for N sample are much

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higher than those of EO sample while the values of ϵ' for NEO sample are in between them. On the other hand, the values of ϵ' and $\tan \delta$ for the EO sample are lower than those for EA sample. This could be attributed to steric hindrance due to the presence of the CH_3 -group in the ortho- position. This restricts the rotation of the OH-group and hinders the association. The variation of $\tan \delta$ versus $\log f$ shows an absorption maximum at about 1 kHz. Similarly, this absorption region could be attributed to Maxwell-Wagner effect.

The effect of higher temperatures on the dielectric properties of these samples has been also studied and the results are represented by dashed lines on Fig. 3. It is clear from these results that both ϵ' and $\tan \delta$ for EO sample are slightly decreased and are not temperature dependent compared with the other samples. It is evident also from the results that high temperatures have no effect on the constitution of the samples similar to what was found before for the EA and NEA samples.

IV. Novolac N, Epoxy Resin EC and Their Mixture NEC:

For N, EC and NEC samples, the frequency dependence of ϵ' and $\tan \delta$ at various temperatures are shown in Fig. 4. It is evident from these data that ϵ' is decreased by increasing the applied frequency f . The rate of this decrease becomes higher with the increase in temperature. It is apparent also that ϵ' for NEC sample is between those of N and EC samples.

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From the variation of $\tan \delta$ versus $\log f$, a loss peak is observed and becomes higher with the increase of temperature. No detectable current is seen to flow through the samples, indicating that they have no d.c. conductivity.

The effect of higher temperatures on the dielectric properties of these samples has been studied and the results are represented by dashed lines in Fig. 4. The interpretation of these results is similar to the given for N, EA and NEA samples.

CONCLUSIONS

1. Thermal stability of epoxy resins is improved in the presence of novolac phenol formaldehyde resin.
2. Thermal stability of all epoxy samples is decreased with the increase of methyl and hydroxyl group percentages.
3. Standard and prepared novolac resins have almost the same dielectric properties.
4. The permittivity of epoxy resins is improved by the addition of novolac resin.
5. No direct current is seen to flow through all the samples, indicating that they have no d.c. conductivity.
6. Epoxy resin prepared from o-cresol acquires very small values of permittivity and power factor as compared with other samples.

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7. Thermal heating of all samples except for that of o-cresol epoxy resin shows a large decrease in the permittivity and power factor.
8. Thermal heating does not show any effect on the constitution of the investigated samples.

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Captions of figures

Fig.1. Permittivity (ϵ') and power factor ($\tan \delta$) versus frequency (f) for (a) standard and (b) prepared novolac resins at different temperatures.

● 30°, x 40°, o 50°C.

Fig.2. Permittivity (ϵ') and power factor ($\tan \delta$) versus frequency (f) for N, EA and NEA samples at different temperatures (——) before and (-----) after heating at 180 - 200 C for 250 hours.

● 30°, x 40°, o 50°, and Δ 60° C.

Fig.3. Permittivity (ϵ') and power factor ($\tan \delta$) versus frequency (f) for N, EO and NEO samples at different temperatures before and after heating.

same notations as in Fig.2.

Fig.4. Permittivity (ϵ') and power factor ($\tan \delta$) versus frequency (f) for N, EC and NEC samples at different temperatures before and after heating.

same notations as in Fig.2.

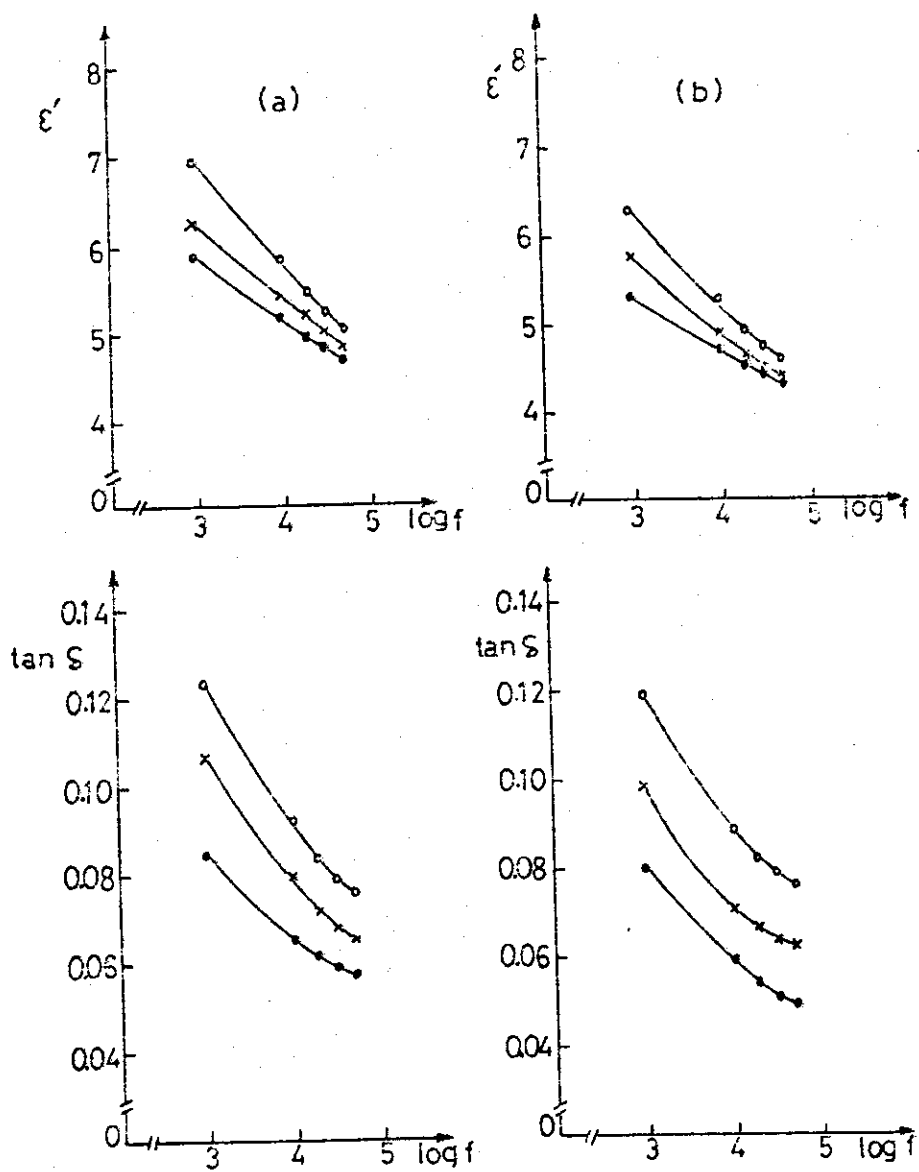


Fig .1.

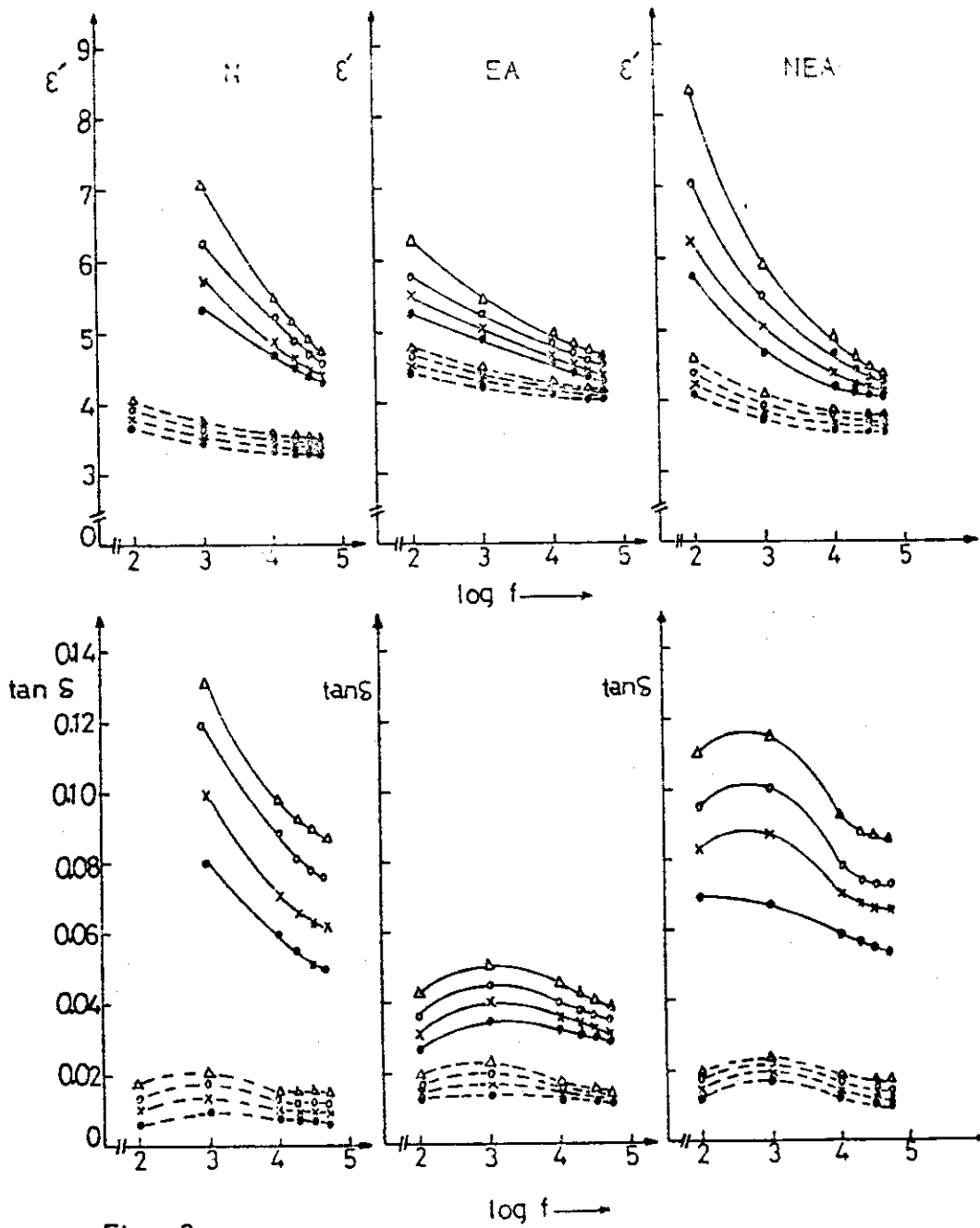


Fig .2.

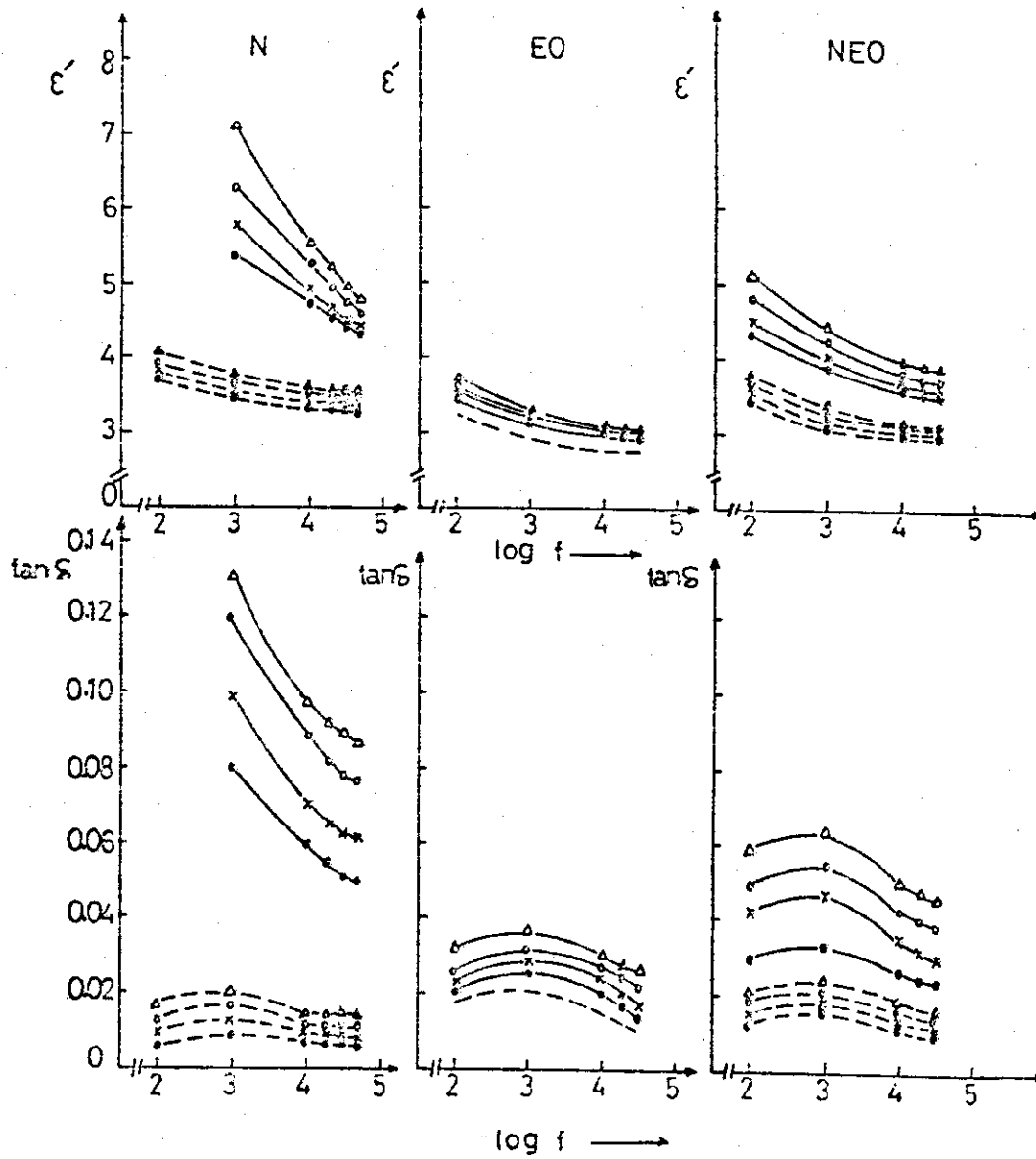


Fig .3.

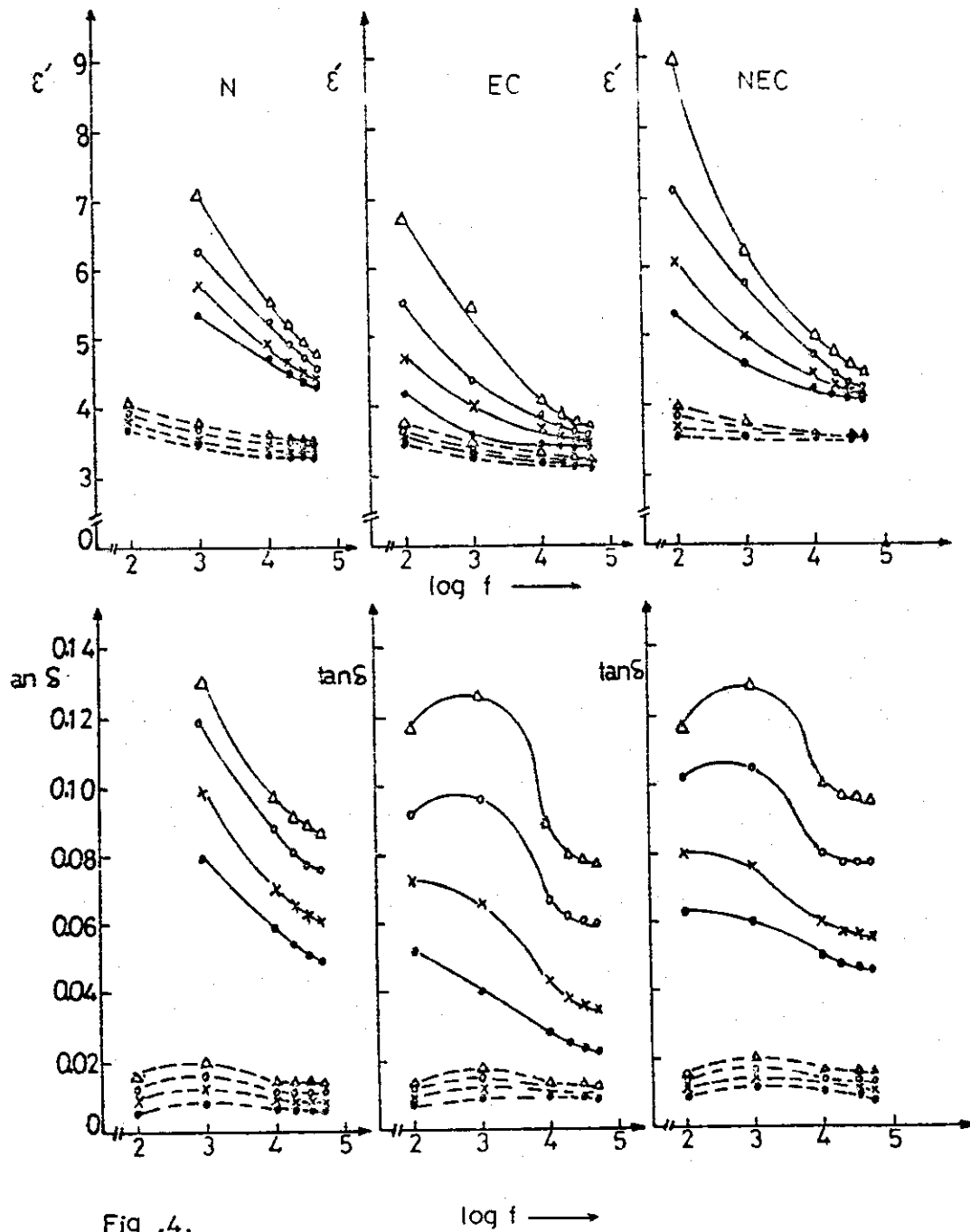


Fig .4.

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