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Dielectric Behavior of Curing Phenolic-Formal Resins

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Synopsis

Dielectric properties of phenolic-formal resins are studied between 0.06 and 300 kHz. The resins are prepared from novolac and 1,3-dioxalane with a strong acid as catalyst. The high dielectric losses are attributed to proton jumps felicitated by water molecules which are produced in the curing reaction. The activation energy of the dielectric relaxation is 0.77 e.v. Curing often continues for weeks after preparation, which is reflected by a gradual increase of the frequency of maximum loss. Drying the samples causes the loss maximum to return to lower frequencies.

Introduction

The dielectric properties of thermosetting phenolic resins are well known. Resole resins, which are prepared from phenol and formaldehyde in a one-stage process, have[1] relative dielectric constants $\kappa' = 5$–10, and loss tangents $\tan \delta = \kappa''/\kappa' = 0.01$–$0.20$. Two-stage phenolic resins are prepared from novolac, which consists of uncrosslinked chain molecules formed at low formaldehyde/phenol ratios. The crosslinked resins are then usually prepared with hexamethylenetetramine as a curing agent. The two-stage resins have[2] dielectric constants $\kappa' = 3.80$–4.35 and $\tan \delta = 0.01$–0.025.

This paper considers the dielectric behavior of a new type of phenolic resins developed by Heslinga and Schors.[3] The preparation involves curing novolac with cyclic formals and an acid as catalyst at low temperatures and under very low pressures. The dielectric investigations were restricted to formal phenolic resins prepared from novolac and 1,3-dioxalane with a mixture of *o*- and *p*-phenolsulfonic acid as catalyst. The dioxalane seems to decompose during the reaction and is almost completely integrated in the resin.[3]

Since it is interesting to know how long curing continues, dielectric measurements were carried out on samples soon after preparation and for periods up to 25 days. Also, the effect of acid concentration was investigated.

Experimental Procedure

Dielectric measurements between 0.06 and 300 kHz* were performed with a Schering bridge (Rohde and Schwarz). Samples with a diameter

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* Here, Hz stands for cycles/sec. in accordance with a recommendation made by the I.U.P.A.P.

of 4.5 cm. and 0.2 cm. in thickness were placed in a condenser with guard ring. The temperature could be controlled by means of an air jacket around the sample holder.

The samples were sawed from sheets which were formed during preparation. They are characterized by the percentage of acid catalyst, the curing temperature, and the time required for preparation. These data will be indicated in parenthesis, e.g. (1%, 80°C., 3 hr.).

Results

Figure 1 shows dielectric constant and loss factor of the novolac used for preparing phenolic-formal resins. The observed values agree almost exactly with those quoted by Carswell.[2] The loss factor κ'' displays a beginning increase toward higher frequencies. This increase is part of a loss area (in the megahertz region) caused by hydroxyl groups.

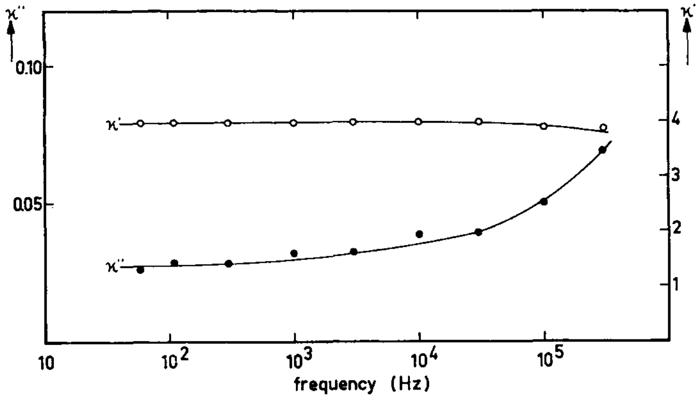

Fig. 1. Dependence of dielectric constant and loss factor of novolac upon frequency.

The dielectric loss curves of the phenolic-formal resins are all broader than simple Debye curves. This is taken into account[4] by introduction of the Fuoss-Kirkwood parameter β, so that

$$\kappa'' = \kappa_m''/\cosh[\beta \ln(\nu/\nu_m)] \quad (1)$$

where ν_m is the frequency of maximum loss. Equation (1) becomes the simple Debye equation when $\beta = 1$. For broader curves, $0 < \beta < 1$, which means that the dielectric dispersion can no longer be described by one single relaxation time. The maximum loss factor κ_m'' is given by

$$\kappa_m'' = \beta(\kappa_s - \kappa_\infty)/2 \quad (2)$$

where κ_s and κ_∞ are the limiting dielectric constants at frequencies very much lower and higher than ν_m, respectively.

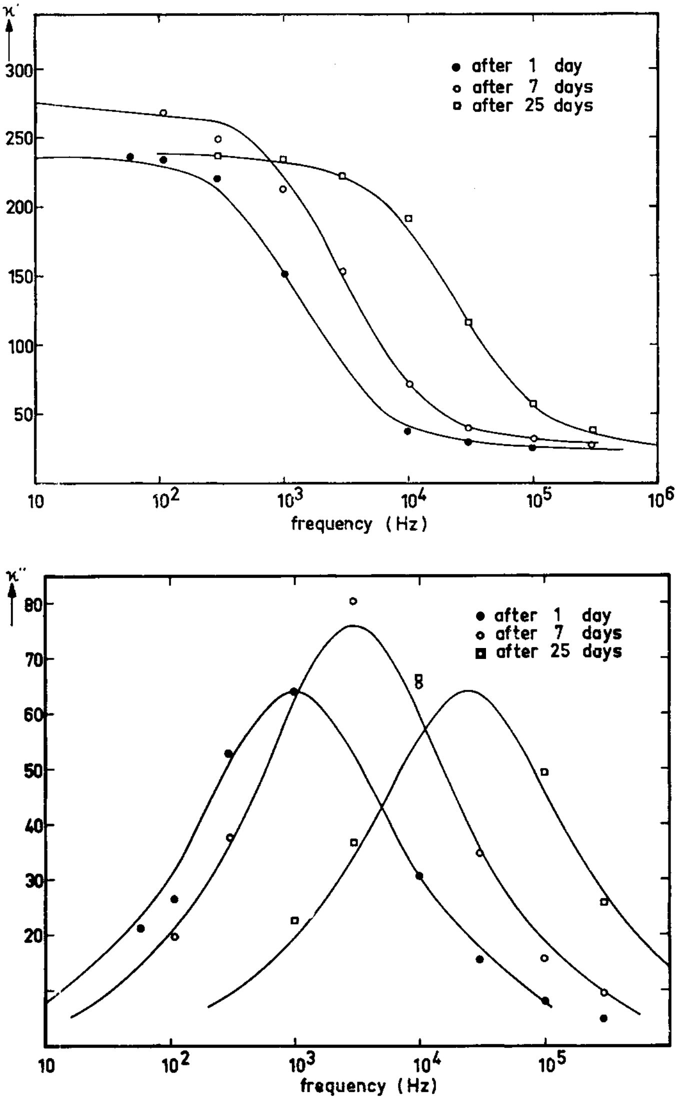

Fig. 2. Frequency dependence of (*a*) the dielectric constant of a resin containing 1% of acid catalyst, measured 1, 7, and 25 days after preparation; (*b*) the loss factor of the resin of Fig. 2*a*. The curves are calculated broadened Debye loss curves.

The first series of resins studied was prepared at 80°C. with 1% acid for different lengths of time. The samples were then stored at 20°C. and 65% R.H. for two days. This was done, because the resins appear to be hygroscopic for some time immediately after preparation. They were dried with filter paper until they did not seem to become humid any more. The measurements were carried out on two consecutive days. Results are given in Table I.

TABLE I

Limiting Dielectric Constants κ_s and κ_∞, Fuoss-Kirkwood Parameters β, Maximum Loss Factors κ_m'' and Frequencies of Maximum Loss ν_m of Samples (1%, 80°C., Different Preparation Times)

Preparation time, min.	κ_s	κ_∞	β	κ_m''	ν_m, kHz
10	—	8.5	0.85	~18	~3
30	—	9.5	0.85	~45	~3
60	93	11	0.85	35	8
90	114	11	0.85	44	8
120	111	11	0.85	42	8
180	113	11	0.85	43	8
240	113	11	0.85	43	8
300	114	11	0.85	44	8

Samples (1%, 80°C., 10 min.) and (1%, 80°C., 30 min.) had very high losses at low frequencies owing to d.c. conductivity. Remarkably, the samples with preparation times larger than 90 min. all had about the same dielectric constants and loss with the same β value and the same ν_m. This is the more surprising, because the curing reaction appears to continue at room temperatures long after preparation.

This is illustrated in Figure 2, which shows dielectric constants and loss factors of a sample (1%, 80°C., 3 hr.) one day, one week, and more than three weeks after preparation. The solid lines are theoretical curves, calculated from eqs. (1) and (2) with the parameters given in Table II. This sample had a much higher loss than those of Table I. This is not unusual in substances containing variable concentrations of ionic compounds.

Table II shows that the dielectric constants and loss factors do not change significantly after preparation. The variations observed are probably caused by experimental errors, which may become as large as 25% for the apparatus used when the maximum losses are as high as in this sample. The frequency of maximum loss seems gradually to move to higher fre-

TABLE II

Dielectric Parameters of a Sample (1%, 80°C., 3 hr.) at Different Times after Preparation

Days after preparation	κ_s	κ_∞	β	κ_m''	ν_m, kHz
1	238	24	0.60	64	1.2
2	230	24	0.60	62	1.75
4	260	24	0.60	61	2.5
7	276	24	0.60	71	3.0
14	300	24	0.60	76	12
25	238	24	0.60	64	24

quencies at 20°C. and 65% R.H. Even after 25 days this motion had not ceased.

Figure 3 shows some examples of loss curves obtained for samples (80°C., 3 hr.) containing different percentages of acid. The solid lines are again calculated loss curves. The dotted line follows experimental points measured at low frequencies for sample (2%, 80°C., 3 hr.) indicating d.c. conductivity and perhaps a second loss region. Results are collected in Table III.

TABLE III
Influence of Different Acid Concentrations on the Dielectric Parameters of Samples (80°C., 3 hr.)

Acid concn., %	κ_s	κ_∞	β	κ_m''	ν_m, kHz
0.25	85	5	0.75	30	0.5
0.50	59	11	0.75	18	3.0
0.75	73	9	0.75	24	5.0
1.00	40	10	0.75	11	17
2.00	46	12	0.75	13	140

The dielectric constants and loss factors appear to vary in a random way, but the critical frequency ν_m increases with the acid concentration.

The parameter β seems to be constant for samples prepared in the same series and is apparently determined by conditions during formation of the sheets.

For further investigations of the observed changes in critical frequency, samples were prepared at 80°C. in which the preparation times and the acid concentrations were varied. In addition, the effect of drying was studied. The results are summarized in Table IV.

TABLE IV
Frequencies of Maximum Loss ν_m in Samples Prepared at 80°C.

	ν_m, kHz			
Acid concn., %	(80°C., 2 hr.)	(80°C., 3 hr.)	(80°C., 6.5 hr.)	(80°C., 6.5 hr.) dried for 17 days
0.25	—	0.5	0.55	0.3
0.50	2.0	3.0	2.5	1.2
0.75	—	5.0	8.5	1.7
1.00	5.0	17	25	3.0
2.00	45	140	2 and 100	0.4 and 30

After preparation the samples were kept at 20°C. and 65% R.H. for about 12 hr. Following the dielectric measurements, samples (80°C., 3 hr.) were further cured at 80°C. for 3.5 hr. to give samples (80°C., 6.5 hr.).

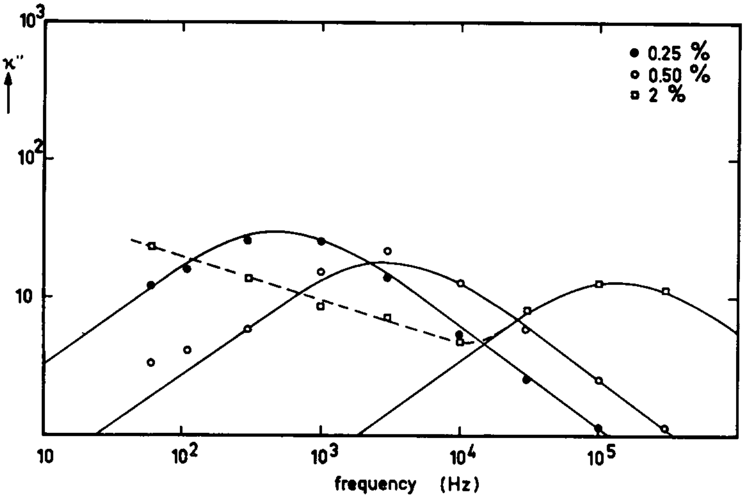

Fig. 3. Dependence of loss factors upon frequency of resins containing 0.25, 0.50, and 2% of acid catalyst. The solid lines are calculated broadened Debye loss curves.

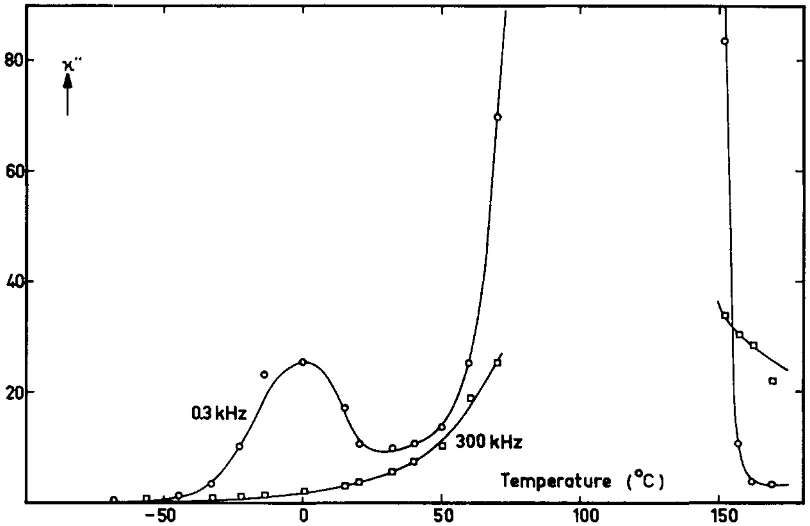

Fig. 4. Temperature dependence of the loss factor (at 0.3 and at 300 kHz) of a resin containing 1% of acid catalyst.

After measuring these they were stored in a desiccator above P_2O_5 for 17 days.

Table IV indicates that the dielectric behavior becomes more complicated in samples containing 2% of acid. Samples (2%, 80°C., 6.5 hr.) had two loss maxima, which were not further studied. The critical frequency increases with the percentage of acid. It also increases with the time of curing at 80°C. A similar but more slow process was observed at room temperature, as shown in Table II. The last column of Table IV shows that ν_m returns to lower frequencies when the samples are dried. The same phenomenon was observed for the samples of Table II. As long as some curing continues ν_m can be moved up and down by alternate drying and exposure to 65% R.H. of the samples.

Figure 4 shows dielectric loss factors of a sample (1%, 80°C., 3 hr.) as a function of temperature at 0.3 and at 300 kHz. Maximum loss at 0.3 kHz is found at 0°C. There is a large increase in loss above 60°C. and it could not be measured between 70 and 150°C. A decreasing loss was observed above 150°C. The material turned black as a consequence of the heat treatment. Its dielectric loss at room temperature had become much smaller than before, and the dielectric constant κ_s was about 20.

Finally the dielectric behavior of some samples (1%, 80°C., 3 hr.) and (1.5%, 80°C., 1.5 hr.) was studied between −20 and 40°C. If the frequency of maximum loss is determined by an equation of the type ν_m = const. exp $(-A/RT)$, a free energy of activation A can be derived by plotting ln ν_m against $1/RT$. All the samples studied had the same activation energy of 0.77 e.v. (= 18 kcal./mole).

Discussion

The frequency of maximum loss ν_m appears to be the most interesting dielectric parameter. It moves to higher frequencies when the acid concentration becomes greater. In addition, it increases in time after preparation as a consequence of continued curing. The curing reaction appears to continue at room temperature for several weeks in the samples studied. Drying reverses the motion of ν_m, and it is possible to move ν_m up and down by alternate vacuum drying and normal storage. Evidently water plays a role in the dielectric loss mechanism. Water molecules are indeed formed during the crosslinking reaction.

However, the observed loss cannot be caused by water alone. Drying does not decrease the height of the loss curve, nor does the height increase on further curing. This seems to exclude dipolar loss of water molecules or, for the same reasons, loss due to polar crosslinks. In both cases one would expect loss to increase as long as curing progresses.

Another possibility would be that water droplets produce a Maxwell-Wagner effect. In that case ν_m would be determined by the conductivity of the enclosed water[5] and should not change in the way observed. The conclusion must therefore be that water plays an indirect part in the loss mechanism.

Dipolar loss in the resin is equally unlikely. The hydroxyl groups have a loss maximum in the megahertz region. Its beginning was found in novolac and also in some of the phenolic-formal resins studied at about 10 kHz.

The only remaining possibility appears to be that the acid catalyst is responsible for the observed dielectric loss. The influence of the catalyst on the electrical properties was clearly discernible in the d.c. conductivity.

At constant applied voltage the current decreased for many hours. The d.c. resistivities were of the order of 10^8 ohm-cm. Ionic dielectric losses have been observed in several substances. Protonic losses in ice were studied by Gränicher, Jaccard, Scherrer, and Steinemann.[6] For a more quantitative treatment of the results, these authors made use of a general result derived by Fröhlich.[7] When N particles of charge e jump under the influence of the field between equilibrium positions separated by an average square distance x^2,

$$\kappa_s - \kappa_\infty = Ne^2x^2/2\,\epsilon_0 kT \tag{3}$$

where $\epsilon_0 = 8.85$ pF./m. is the dielectric constant of vacuum. The data in Table II give an average value of $(\kappa_s - \kappa_\infty) = 230$. Insertion of this value in eq. (3) leads to $Nx^2 = 6.4 \times 10^8$ m.$^{-1}$.

A resin sample (1%) contains about 0.015 g. of acid (M.W. = 172)/cm.^{3}. When complete dissociation is assumed this gives $N = 5.2 \times 10^{25}$ protons/m.^{3}. As an estimate of the distance between protons we take $N^{-1/3} = 2.7 \times 10^{-9}$ m. (= 27 A.). In this approximation $Nx^2 = 3.7 \times 10^8$ m.$^{-1}$, in reasonable agreement with the value 6.4×10^8 derived from the dielectric data. The agreement could be made even better by choosing the data from Table I for comparison, where $(\kappa_s - \kappa_\infty) = 100$.

The activation energy of 0.77 e.v. seems to be acceptable in comparison with other ionic loss data. Auty and Cole found 0.57 e.v. in ice,[8] and Volger, Stevels, and Van Amerongen correlated 0.75 e.v. with motions of sodium ions in glass.[9]

A protonic loss mechanism can also account for other observations. The formation of water molecules in the curing process appears to facilitate proton jumps. Water does not contribute to the height of the loss, it only provides the protons with stepping stones. Formation of more water eases the motions and moves the loss maximum to higher frequencies. Drying, on the other hand, moves the maximum back.

Heating to temperatures above 100°C. removes the enclosed water and terminates the curing reactions. Heat-treated samples had completely lost the peculiar dielectric properties ascribed to proton jumps.

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Résumé

Les propriétés diélectriques de résins phénol-formal ont été étudiées aux fréquences de 0.06 à 300 kHz. Les résines ont été préparées à partir de novolac et de 1,3-dioxalane avec un acide fort comme catalyseur. Les pertes diélectriques élevées sont attribuées à des mouvements protoniques facilités par des molécules d'eau produites pendant la réaction durcissante. L'énergie d'activation est de 0.77 e.v. Le durcissement continue souvent pendant quelques semaines après la préparation et se traduit par une augmentation graduelle de la perte maximum. Le maximum se déplace vers les fréquences moins élevées après séchange des échantillons.

Zusammenfassung

Dielektrische Eigenschaften von Phenol-Formal-Harzen werden zwischen 0,06 und 300 kHz untersucht. Die Harze wurden aus Novolak und 1,3-Dioxalan mit einer starken Säure als Katalysator hergestellt. Die hohen dielektrischen Verluste werden einem durch die bei der Härtungsreaktion gebildeten Wassermoleküle erleichterten Protonsprungmechanismus zugeschrieben. Die Aktivierungsenergie der dielektrischen Relaxation ist 0,77 eV. Die Härtung geht oft nach der Herstellung noch einige Wochen weiter und kann an einer allmählichen Verschiebung des Verlustmaximums nach höheren Frequenzen verfolgt werden. Das Verlustmaximum kehrt bei Trocknung der Proben zu niedrigeren Frequenzen zurück.

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