

pole rotation are the same in both cases. Apparently the chlorodiphenyl molecules are locked into an arbitrary distribution by the surrounding polymeric chains. It will be interesting to study other polar solutes in non-polar polymers in order to determine the effect of size and shape of the solute molecule on a. c. properties.

The identity of the field sensitive groups in the two systems discussed above is confirmed by the heights of the absorption maxima: they are proportional to the chlorine content, as shown in Table IV. This result is clear proof that the a. c. properties of polar polymers are due to the response of the dipoles to the field, and the identity of the polar group in the polymer is established.

TABLE IV
ABSORPTION MAXIMA IN CHLORINE SYSTEMS

System	% Cl	ϵ''_{\max}	$\epsilon''/\%$
Polystyrene-chlorodiphenyl 90:10	1.88	0.021	1.12
Polystyrene-chlorodiphenyl 80:20	3.76	0.047	1.25
Polychlorostyrene-diphenyl 80:20	20.5	0.305	1.50

Summary

1. The a. c. properties at 60–10,000 cycles over a wide temperature range have been determined for the following systems: polyvinyl chloride;

polyvinyl chloride–diphenyl 80:20; polystyrene; polystyrene–*p*-chlorodiphenyl 90:10 and 80:20; poly-*p*-chlorostyrene, alone and with various amounts of diphenyl, *o*-chlorodiphenyl, *p*-chlorodiphenyl and mixtures of the last two.

2. The above systems show characteristic maxima in absorption and dispersion in dielectric constant, which are determined by the size and strength of the polar group, by the length and flexibility of the bond of the polar group to the polymer chain, and by the nature and amount of a second component present as plasticizer.

3. The fundamental mechanism of a. c. response is dipole rotation in a medium of high viscosity; it differs from the mechanism obtaining in ordinary polar liquids in that simple rotatory Brownian motion must be replaced by internal rotatory Brownian motion related to the change in convolutions of the polymeric chain.

4. The primary effect of changing temperature is to change the internal viscosity.

5. A transition temperature has been found in the case of polyvinyl chloride at which a process best described as an internal melting occurs.

SCHENECTADY, N. Y.

RECEIVED MAY 7, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Electrical Properties of Solids. VII. The System Polyvinyl Chloride–Diphenyl

By RAYMOND M. FUOSS

I. Introduction

A plastic containing 20 parts diphenyl and 80 parts polyvinyl chloride by weight was described in the previous paper of this series.¹ Its properties differed markedly from those of polyvinyl chloride alone: The value of the high temperature–low frequency dielectric constant was lowered, the absorption peak for a given frequency was shifted to lower temperatures by about 60° (which corresponds to many decades change in viscosity), and the shapes of the low temperature dielectric constant and loss factor curves were completely altered. Polyvinyl chloride shows a minimum in 60 cycle loss factor at 65° which is located between a broad low maximum at 0° and a sharp high one at 98°, while the curve for P-ViCl-Ph₂ 80:20 has a sharp high maximum at

42.5°, and is monotone, descending from there to –70°, with no indication of a low temperature maximum. These differences all suggested that it would be interesting to explore the range 0–20% diphenyl in some detail, in order to see how the transitions occurred.

The most striking result of the investigation was the non-linearity of the properties of the system in composition. As far as the low temperature changes are concerned, about half of the transition from the curve characteristic of polyvinyl chloride to that for the 80:20 system occurs with the addition of the first 5% diphenyl, and about one-third with only the first 1% diphenyl in the plastic. One per cent. diphenyl corresponds roughly to one diphenyl molecule to 250 monomeric (–CH₂CHCl–) units. The high temperature properties also change rapidly with the first

(1) FUOSS, THIS JOURNAL, 63, 369 (1941).

5-6% diphenyl; after that, the maximum in $\tan \delta$ (which is the ratio of loss factor to dielectric constant) is practically independent of composition. The general impression one obtains is that the first additions are relatively very efficient in changing the electrical properties, by separating polymeric chains, but eventually further addition of diphenyl corresponds simply to adding diphenyl molecules between previous molecules which already have broken the coupling of adjacent polymeric chains, and consequently the later additions are much less effective. To use the previous analogy of plasticized polymers to solutions, after the first few per cent. of diphenyl, the system is in the dilute solution range where properties are simple, while up to the first few per cent., we are going through the *concentrated* range of solutions of polyvinyl chloride in diphenyl. For example, for a molecular weight of 30,000 for the polymer, only 0.5% diphenyl is required for an equimolar solution, and 5% diphenyl corresponds to approximately one mole of polymer in 10 of diphenyl.

II. Materials, Apparatus, Method

The polyvinyl chloride was the same low molecular weight material, extracted with alcohol, which was used in the work for the preceding paper. Diphenyl was twice recrystallized from alcohol; m. p. 69.0°. Measurements from 60 to 500 cycles were made on the Schering bridge, and from one to 10 kilocycles on the parallel bridge. Samples were 5-cm. disks, about 2 mm. thick, faced with aqua-dag electrodes. They were measured in the three terminal platinum cell.

Samples were prepared by dissolving diphenyl in petroleum ether (b. p. $\leq 50^\circ$), adding the solution to the polyvinyl chloride and stirring during the evaporation of the solvent. The resulting material was sheeted at 100° several times to complete mixing, and then disks were pressed from the sheeted plastic for five minutes at 130°, in a closed mold.

Specific volumes were determined from the dimensions of the disks and their weights; for 0-15% diphenyl

$$v = 0.713 + 0.187p/100 \quad (1)$$

where p is the percentage of diphenyl in the plastic. Eq. (1) corresponds to a slight contraction when diphenyl ($v = 0.961$) and polyvinyl chloride are mixed.

A series of samples were made containing up to 40% diphenyl. All were transparent and homo-

geneous when above the melting point of diphenyl; on cooling to room temperature, the samples containing 25-40% diphenyl became opalescent or opaque white. From 20% down, however, the samples were transparent, and stayed so, even after long immersion in petroleum ether chilled to -70° with dry-ice. We conclude that the composition-temperature diagram for the system $PVCl-Ph_2$ contains a region of limited solubility, with an upper consolute temperature somewhere between 30° and 70°.

The samples containing 0-15% diphenyl did not shrink in diameter at room temperature, after being taken out of the mold, while those which contained 20% or more shrank several per cent. in diameter. This observation means that the brittle point for 0-15% is about 30° or higher, and for 20% up is below 30°. Again we find a correlation between mechanical and electrical properties. The sharp rise in a. c. absorption appears at 30° for the 15% sample, at 20° for 20% and at 35° for 12%. This rise in absorption accompanies a transition which we have described as an internal melting² which occurs at the brittle point. In an ordinary solid, a three-dimensional force network is broken at the melting point and is replaced by one of much weaker forces. In the plastic solid, forces in the two dimensions perpendicular to the chain axis drop in magnitude at the brittle point, but along the chain axis, the bonds are still primary valence bonds.

Two further deductions from experimental methods might be mentioned here. The fact that the addition of only 1% diphenyl made an enormous change in the low temperature $\epsilon''-T$ curve for polyvinyl chloride is clear proof that the original polymer was free from traces of low molecular weight impurities. Second, the fact that the properties (ϵ' or ϵ'') at a given temperature and frequency gave smooth curves when plotted against composition argues for the uniformity of the plastics made by the petroleum-ether method.

III. Experimental Results

The experimental results are summarized in tabular form, as American Documentation Institute Document No. 1460.* Space was not avail-

(2) E. Mack, *J. Phys. Chem.*, **41**, 221 (1937), has used the phrase "internal melting point" in describing partial rupture of lattice bonds in other systems.

* For a copy of the tables, order Document 1460 from the American Documentation Institute, Offices of Science Service, 2101 Constitution Ave., Washington, D. C., remitting 33¢ for microfilm or \$1.50 for photocopies readable without optical aid.

able for their reproduction here. Dielectric constants and loss factors are given as functions of frequency (60 cycles to 10 kilocycles) and temperature (-70° to $+100^{\circ}$), for the different plastics studied (0 to 15% diphenyl by weight).

As before, the a. c. loss factor ϵ'' is calculated by subtracting the measured d. c. conductance κ_0 from the total a. c. conductance at frequency f , and then multiplying the difference by $2 \times 9 \times 10^{11}/f$.

$$\kappa_f - \kappa_0 = \epsilon''f/180 \times 10^{10} \quad (2)$$

We point out again that this simple method of correcting for the presence of electrolyte is only a first approximation. It removes an exponential blow-up in the $\epsilon''-T$ curves for low frequencies and high temperatures but still leaves a term which becomes zero with increasing frequency approximately as $(1/\sqrt{f})$. Further work with electrolytes in plastic solvents will be necessary before the non-electrolytic a. c. loss can be correctly calculated from the total and d. c. conductances. Some

very interesting polarization effects are anticipated.

The data contained in the tables serve to map the two components of the complex quantity

$$\epsilon = \epsilon' - i\epsilon'' \quad (3)$$

as functions of the three independent variables temperature, frequency and composition

$$\epsilon = \epsilon'(T, f, p) - i\epsilon''(T, f, p) \quad (4)$$

The loss factor ϵ'' measures the imaginary part of ϵ which is the part in phase with the applied voltage, while ϵ' , the dielectric constant, measures the real part of ϵ which is 90° ahead of the voltage in phase.

Two-dimensional sections are shown in Figs. 1-6, which may help to visualize the function (4). In Figs. 1 and 2 are shown the real and imaginary components of ϵ for 60 cycles at different compositions as functions of temperature; Figs. 3 and 4 correspond to the fixed composition PViCl-Ph₂ 94:6 at different temperatures as functions of frequency; Fig. 5 gives loss factors at 60 cycles

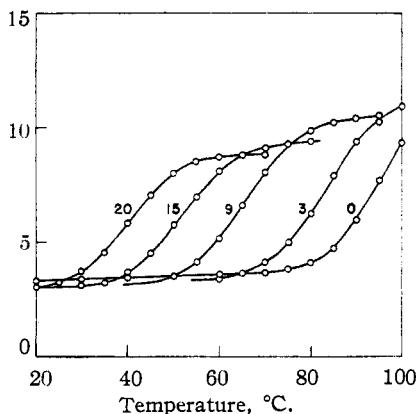


Fig. 1.—Dielectric constants at 60 cycles as functions of temperature and composition.

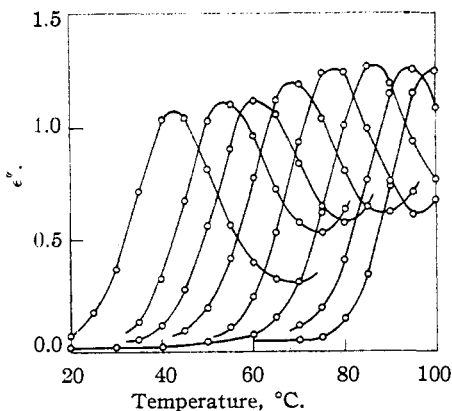


Fig. 2.—Loss factors at 60 cycles; 20, 15, 12, 9, 6, 3, 1.0% Ph₂ left to right.

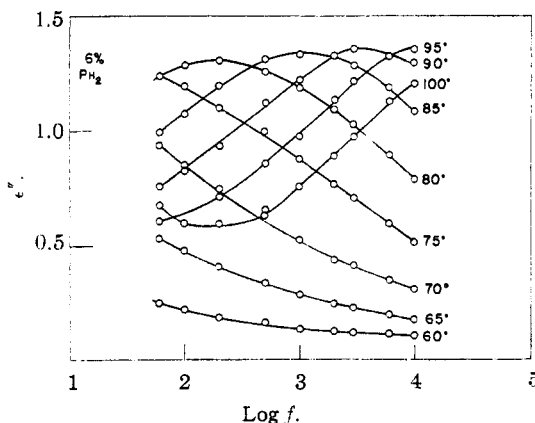


Fig. 3.—Loss factors of PViCl-Ph₂, 94:6.

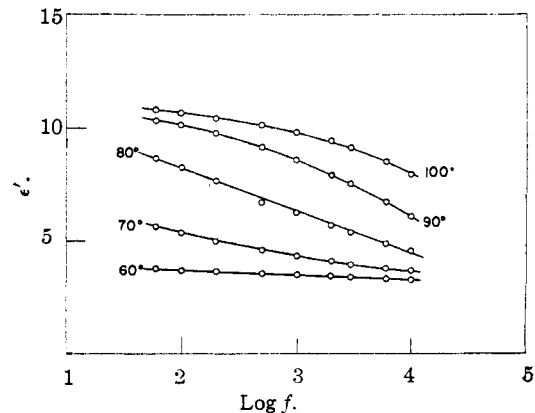


Fig. 4.—Dielectric constants of PViCl-Ph₂, 94:6.

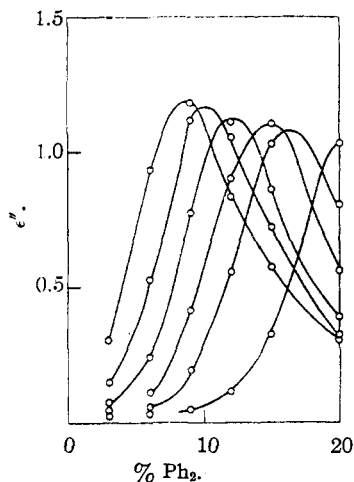


Fig. 5.—Loss factors at 60 cycles: left to right, 70°, 65°, 60°, 55°, 50°, 40°.

and different temperatures as a function of composition; and Fig. 6 is a map in the $\epsilon' - \epsilon''$ plane at fixed composition (6% Ph_2) at different temperatures with frequency as the variable parameter.

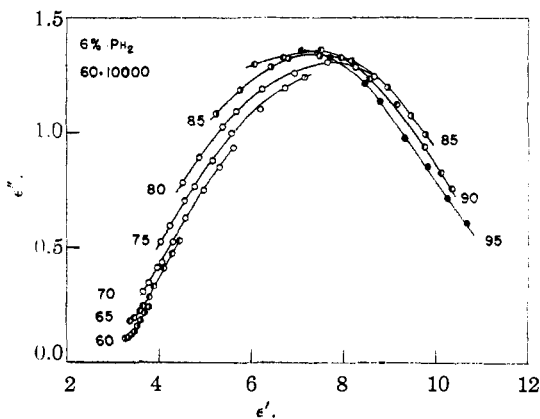


Fig. 6.—Dielectric constant-loss factor map.

IV. Discussion

The striking effect of small amounts of plasticizer on the polymer is best shown in the loss factor-temperature curves at low temperatures. In Fig. 7, we have the 60-cycle ϵ'' values plotted against T , for 0, 1, 3, 6, 12 and 20% diphenyl. It is seen that only 1% lowers the maximum in ϵ'' to 73% of its value for pure polyvinyl chloride, and shifts it from 0 to -25° along the temperature axis. The minimum is shifted from $+65^\circ$ to $+35^\circ$, and is considerably broadened. With increasing amounts of diphenyl the maximum becomes lower, shifts to lower temperatures,

and eventually disappears after the minimum and maximum coalesce to a horizontal inflection. The dielectric constant-temperature curves also show characteristic changes. In the low temperature range, ϵ' is roughly linear in T , and then suddenly rises sharply at the temperature at which the loss factor begins its almost exponential climb. Addition of diphenyl to polyvinyl chloride decreases the slope of the $\epsilon'-T$ curves in the low temperature range, decreases the dielectric constant at a given temperature, and lowers the temperature at which the sharp rise in the $\epsilon'-T$ curve appears.

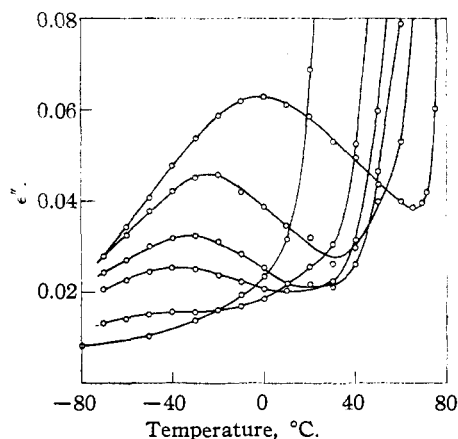


Fig. 7.—Low temperature loss factors at 0, 1, 3, 6, 12 and 20% Ph_2 .

The effect of small amounts of plasticizer suggests that the low temperature absorption is due to a lengthwise coupling between segments of polymeric chains. Then the presence of a diphenyl molecule separates chain lengths considerably greater than merely the length of the diphenyl molecule; in other words, the added molecules act as spacers between the chains, and the first ones added are relatively much more effective in separating the polar chains. It will be very interesting to see how the changes depend on the shape and size of the plasticizer molecule.

All of the samples showed the peculiar creep¹ in properties in the temperature range where the minimum appears. This observation lends support to the idea that some transition is occurring at the temperature in question, and the two maxima in the $\epsilon''-T$ curve really correspond to two quite different states of the polymer. Also, measurements by Dr. D. J. Mead show that the density-temperature coefficient is larger in the high temperature range than in the low by a factor

of two, which suggests that the low temperature phase is a solid, while the high temperature phase is more like a liquid.

The high temperature properties also show a sensitivity to the first plasticizer added, although to a less marked degree than the low temperature properties. For a given frequency, the value of the maximum tangent ($\tan \delta = \epsilon''/\epsilon'$) increases rapidly for the first 5% of diphenyl, and then becomes nearly constant. The 60-cycle loss factor (Fig. 8) goes through a maximum at about 5% diphenyl: that is, ϵ'' increases faster than ϵ' up to 5% plasticizer, and from there on the two decrease at about the same rate with further addition of diphenyl. The main effect of the diphenyl after the first 5% on the high temperature properties is to shift the absorption maximum for a given frequency to lower temperatures, as would be expected if the plasticizer reduces the internal viscosity.

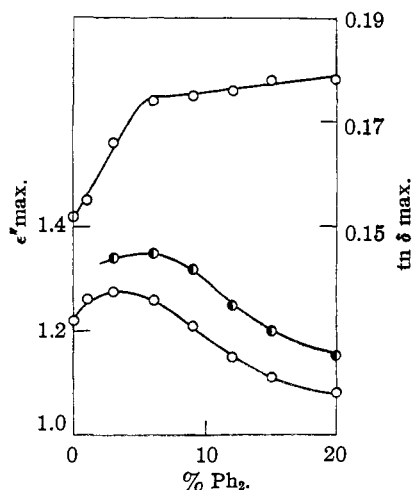


Fig. 8.—Maximum tangent (60~) and maximum loss factor (● 6000~, ○ 60~) as functions of composition.

This conclusion is also borne out by the d. c. data. All the samples had as nearly as possible the same thermal history during their preparation, so the electrolyte content (hydrogen chloride by pyrolysis of the polymer) was presumably about the same in all. A higher d. c. conductance at a given temperature can then be taken to mean a lower viscosity, and the data show that the d. c. conductance increases rapidly with diphenyl content at a given temperature. Furthermore, for a given composition, the logarithm of the d. c. conductance κ_0 is linear in $1/T$, as is shown in Fig. 9.

If we set

$$\log \kappa_0 = A - Q/RT \quad (5)$$

the Q values run from 64 kcal. for polyvinyl chloride to 39 for PVCl-Ph₂, 80:20, approximately linear on a Q - $\log p$ plot from $p = 3$ to $p = 20$.

For a given frequency, the loss factor maximum shifts to lower temperatures as the diphenyl content increases. But the d. c. conductance for different samples at the different temperatures at which their maxima occur are all the same. Table I shows the results; t_m is the temperature at which the maximum in the 60-cycle tangent appears.

TABLE I

D. C. CONDUCTANCE AND A. C. ABSORPTION		
% Ph ₂	t_m	$-\log \kappa_0$
1	91	12.9
3	83	12.9
6	74	13.0
9	65	13.1
12	58	12.9
15	50	13.0
20	40	13.0

In other words, the viscosity, as measured by the d. c. conductance, is the same for different samples at the temperatures corresponding to their peak loss at a given frequency, so there must exist a relaxation mechanism controlled by a viscosity.

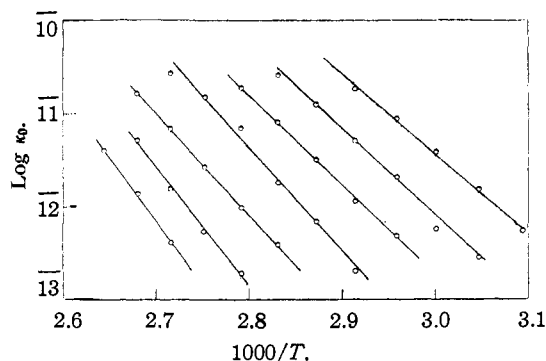


Fig. 9.—D. c. conductances: left to right, 1, 3, 6, 9, 12, 15, 20% Ph₂.

The mechanism is not describable in terms of a single relaxation time, because the ϵ'' - $\log f$ and ϵ' - $\log f$ curves do not have the shape predicted by Debye's theory, and also the value of ϵ'' at its maximum is much less than half the difference between the high temperature dielectric constant and the square of the index of refraction ($n \approx 1.55$, nearly independent of composition in the 0-20% range). A very pretty test plot is ob-

tained by plotting $\epsilon''/2\epsilon''_{\max}$ against $(\epsilon' - n^2)/2\epsilon''_{\max}$, with frequency or temperature as a parameter. For a simple system characterized by a single time of relaxation a semicircle will result. For the PViCl-Ph₂ systems, an unsymmetrical arc, which is much broader than a semicircle, is obtained.

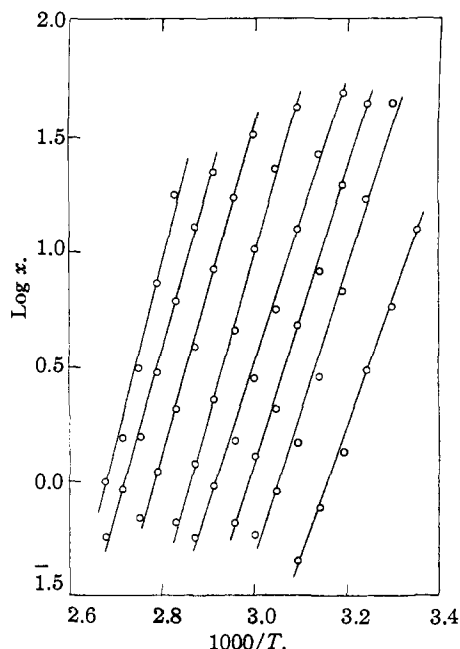


Fig. 10.—Viscosity test plot, left to right: 0, 1, 3, 6, 9, 12, 15, 20% Ph₂.

If, however, a variable x is defined by the equation

$$\epsilon''/2\epsilon''_{\max} = x/(1 + x^2) \quad (6)$$

we find

$$\log x = A' + Q'/RT \quad (7)$$

as is shown in Fig. 10. The slopes (at 60 cycles) run from $Q' = 35$ kcal. for PViCl to 25 kcal. for the 80:20 system. Q' decreases as the frequency increases. For the 80:20 system at 10 kc. $Q' = 18$ kcal., consequently, a viscosity mechanism is acting, but x of Eq. (6) cannot be interpreted as the Debye $\omega\tau$, where ω is 2π times the frequency, and τ is the relaxation time, because the intercepts A' of Eq. (7) vary much more slowly than $\log \omega$. These results would be expected if ϵ'' were of the form

$$\epsilon'' = \sum B_j x_j / (1 + x_j^2) \quad (8)$$

where

$$x_j = \omega\tau_j \quad (9)$$

and τ_j is a relaxation time characteristic of the j -th species of oscillators present.

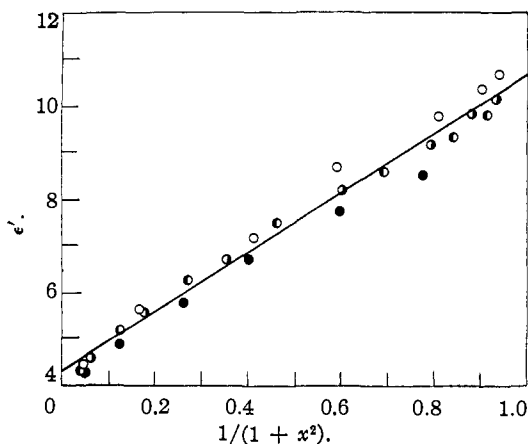


Fig. 11.—Variation of dielectric constant with x :
○, 60~; ◐, 500~; ◑, 1000~; ●, 6000~.

A correlation between ϵ' and ϵ'' values through the x of Eq. (6) can be obtained. If ϵ' is plotted against $(1 + x^2)^{-1}$, straight lines are obtained through the temperature range of the high temperature ϵ'' peak for a given frequency, as is shown in Fig. 11. The slope and intercepts vary somewhat with frequency; for a fixed frequency the points are within the experimental error linear. To prevent confusion, a single average line is drawn in Fig. 11. If we write

$$\epsilon' = \epsilon'_L + (\epsilon'_H - \epsilon'_L)/(1 + x^2) \quad (10)$$

where ϵ'_L is the low temperature limit obtained by extrapolating the $\epsilon' - (1 + x^2)^{-1}$ plots to $x = \infty$, and ϵ'_H is the high temperature limit ($x = 0$), we find the values of Table VII for 60 cycles. It will be noted that

$$\epsilon'_L \gg n^2$$

i. e., the low temperature dielectric constant, as far as the high temperature mechanism is concerned, equals n^2 plus the contribution of the low temperature mechanism to capacity.

TABLE II
DIELECTRIC CONSTANT ANALYSIS

%	ϵ'_L	ϵ'_H	ϵ''_{\max}
0	5.6	12.8	1.22
1	5.5	12.2	1.26
3	4.7	11.6	1.275
6	4.5	11.1	1.26
9	4.4	10.6	1.21
12	4.2	9.9	1.15
15	4.1	9.6	1.11
20	4.1	8.9	1.08

If we calculate dielectric constants by means of Eq. (10) and the data of Table II, and subtract the sum of these calculated values plus the extra-

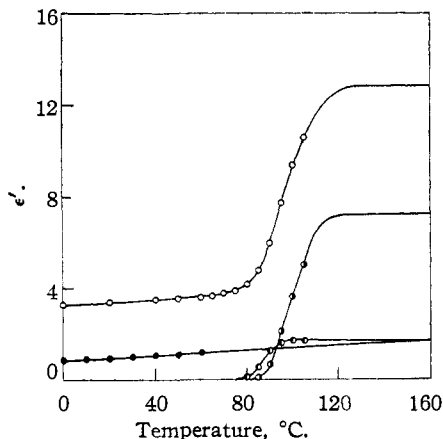


Fig. 12.—Dielectric constants of polyvinyl chloride at 60 cycles: O, observed; ●, ϵ'_1 ; ○, ϵ'_2 ; ●, ϵ'_x .

polated low temperature dielectric constants from the observed high temperature dielectric constants, another absorbing mechanism is revealed. Such an analysis is shown in Fig. 12 for polyvinyl chloride. The dielectric constant appears to be the sum of four terms, as follows

$$\epsilon' = n^2 + \epsilon_1 + \epsilon_2 + \epsilon_x \quad (11)$$

where ϵ_1 is the dielectric contribution of the mechanism which gives the low temperature ϵ'' peak, ϵ_2 is that corresponding to the sharp high temperature maximum in ϵ'' , and ϵ_x is the contribution from an unknown mechanism. It is the presence of ϵ_x which produces the asymmetry in the ϵ'' ϵ' test plots. No suggested explanation for ϵ_x can be ventured at present. It is interesting to note that the high temperature limit of ϵ_x is the same as that for ϵ_1 , and that the ϵ_x absorption band comes at the transition temperature, almost as if the low temperature mechanism suddenly starts to contribute double to the total capacity in the transition range.

If ϵ'_L , ϵ'_H , or ϵ' at ϵ''_{max} for a given frequency is plotted against composition, a concave-up curve is obtained. A similar curve is also obtained when $(\epsilon - 1)v$ is plotted, where v is specific volume. The sharpest curvature appears near $p = 0$; this is another example of the marked non-linearity of the polymer-plasticizer systems in the range of low plasticizer contents.

Very interesting and useful plots are obtained when $\log x$, defined by Eq. (6) for a given frequency and temperature, with composition as the variable, is plotted against $\log (n_2/n_1)$, where n_2/n_1 is the mole ratio of plasticizer to polymer, the latter reckoned as monomer. Straight lines

are obtained, with slopes dependent on temperature. The slope and intercept of these lines furnish for the first time a numerical measure of the effectiveness of a given plasticizer in reducing the viscosity for a given polymer. For example, 10.2 mols of diphenyl to 100 monomer units gives the 60 cycle-40° peak in ϵ'' as a function of composition (Fig. 5), while only 7.6 mols of tricresyl phosphate³ are required to reach the same viscosity. Further work, intended to show how these constants depend on the geometry of the plasticizer molecule, is planned.

Plasticized linear polymers in general exhibit high temperature elasticity⁴; that is, at high temperatures they show plastic flow and have a small Young's modulus, while at low temperatures they behave like elastic solids with a large value of the modulus E . In Fig. 13 are shown values of E as functions of temperature for polyvinyl chloride-diphenyl systems containing 5, 10, 15 and 20% diphenyl.⁵ The black circles on

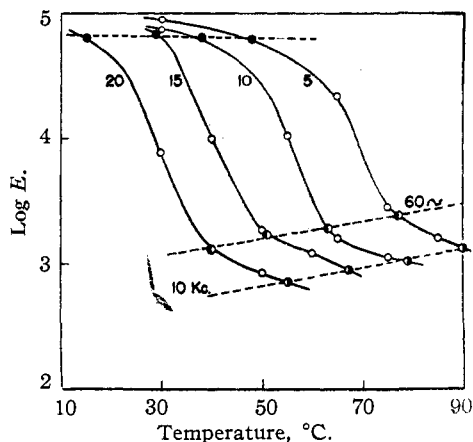


Fig. 13.—Correlation between mechanical and electrical properties.

the upper parts of the curves are the temperatures at which the ascending 60-cycle tangent (Fig. 7) equals 0.015, *i. e.*, about midway through the temperature range where the creep in electrical properties was noted. This is the temperature range where a transition was suspected; we see that it occurs at about the *same* value of modulus for different compositions—just before the high modulus starts its sigmoid drop to low values,

(3) Fuoss, *THIS JOURNAL*, **61**, 2334 (1939).

(4) Kuhn, *Angew. Chem.*, **52**, 289 (1939).

(5) We are indebted to Dr. W. F. Busse, of the Goodrich Company, for these determinations. They were suggested by similar results which he presented at the meeting of the National Research Council Committee on Insulation at Cambridge on November 4, 1939, for polyvinyl chloride-tricresyl phosphate systems.

or in other words, at the transition from brittle to elastic. Furthermore, if we put on the log E - T curves the temperature at which the loss factor for a given frequency reaches its peak, we find that the modulus at the temperature of maximum loss varies by about a factor of two for this range of composition. This is about what would be expected from Maxwell's equation⁶

$$\eta = (1/2) \left(\frac{1}{1 + \mu} \right) E_0 \lambda \quad (12)$$

where η is viscosity, μ is Poisson's ratio, E_0 is the coefficient of Young's modulus in the form $E = E_0 e^{-t/\lambda}$ and λ is the time of elastic relaxation. We previously showed (Table I) that the d. c. conductance was constant at the temperature of maximum absorption for a given frequency for different concentrations of diphenyl and argued that this means equal viscosities. Then if η is constant, we have $E_0 \lambda$ constant, and since λ decreases with increasing temperature, the modulus should increase with increasing temperature, as is actually the case according to the data shown in

(6) Maxwell, *Phil. Mag. J. Sci.*, IV, 35, 134 (1867).

Fig. 13. We hope to find further correlations between electrical and mechanical properties of these systems, which may lead to a clearer understanding of the molecular mechanism involved.

Summary

1. The system polyvinyl chloride-diphenyl has been studied over the ranges -70 to $+100^\circ$, 60 cycles to 10 kilocycles and 0-20% diphenyl.
2. Further evidence that the electrical properties of polar polymers are due to a viscosity controlled relaxation mechanism is given.
3. As a function of composition, the loss factor for a given frequency and temperature goes through a maximum at a concentration which is characteristic of a given plasticizer.
4. The low temperature absorption in polar polymers is reduced and eventually eliminated by the addition of a second component.
5. The electrical properties are markedly non-linear in composition in the low concentration range of compositions.

SCHENECTADY, NEW YORK RECEIVED AUGUST 3, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Electrical Properties of Solids. VIII. Dipole Moments in Polyvinyl Chloride-Diphenyl Systems*

BY RAYMOND M. FUOSS AND JOHN G. KIRKWOOD

I. Introduction.—It is now well known that the electrical properties of polar systems containing giant molecules differ markedly from those in which the dipoles are on small molecules. The properties of the latter are well accounted for by Debye's theory of anomalous dispersion in which the fundamental assumption is a finite time of relaxation, specified by the size and shape of the polar solute molecule and the temperature and viscosity of the solvent. Three characteristic differences between the polymeric systems and the systems describable in terms of a single relaxation time appear: (1) the inflection slopes of the dielectric constant log-frequency curves are much lower in the former; (2) the corresponding loss factor log-frequency curves have a much larger half-width; and (3) the maximum loss factor is always much less than half the difference between

the static dielectric constant and the square of the index of refraction. These differences can all be accounted for by assuming that many times of relaxation rather than a single one are involved. Wagner¹ assumed a Gaussian distribution of relaxation times in order to account for discharge curves, and Yager² has developed a method for applying the Gauss distribution to an analysis of a. c. data. We have, however, no actual proof of the necessity for the existence of a distribution of relaxation times for a given system, nor have we any right to assume that a possible distribution should be Gaussian. In fact, for data on polyvinyl chloride systems³ it has been shown that the Gauss distribution will not reproduce the experimental results.

It is, of course, qualitatively plausible that a system containing a polar polymer should exhibit a distribution of relaxation times, because every di-

* Presented at the Fifth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, Columbia University, New York, December 30, 1940 to January 1, 1941.

(1) Wagner, *Ann. Physik.*, 40, 817 (1913).

(2) Yager, *Physics*, 7, 434 (1936).

(3) Fuoss, *THIS JOURNAL*, 63, 369, 378 (1941).