

Polymer Composites Containing Plasma-Treated Mica.

II. Dielectric Properties

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Synopsis

The complex relative permittivity $K^*(\omega)$ of polymer-mica composites has been studied in the frequency range extending from about 10^{-2} to 10^7 Hz. Microwave plasma treatment in ethylene of the mica flakes leads to significant alterations of $K^*(\omega)$ for three matrix polymers used—polyethylene, polystyrene, and a mixture of these two polymers. The origins of the dispersion characteristics were investigated using a series of polyethylene samples containing up to 50 wt-% of untreated mica. Comparing experimental results with theoretical analyses of the Maxwell-Wagner interfacial polarization effect, it is possible to identify two major contributions to $K^*(\omega)$: a Debye-like dispersion centered near 10^2 Hz and a charge-diffusion mechanism which contributes primarily at low frequencies (≤ 10 Hz).

INTRODUCTION

In the foregoing paper¹ (henceforth referred to as part I), it was shown that surface modification of mica flake by microwave plasma irradiation in ethylene gas using an LMP apparatus (LMP = Large Volume Microwave Plasma Generator; see ref. 2 and part I) could produce significant changes in the properties of the mica as a filler for polyethylene (PE), polystyrene (PS), and mixed PE/PS matrixes. Presumably because of the polymerization of an ethylenic polymer layer on the mica, adhesion at PE/mica interfaces was enhanced by irradiation, but a negative effect was produced at PS/mica interfaces. Rheological and mechanical property variations consistent with this assumption were reported in part I.

Mica has been used for many years as an insulator or dielectric medium, roles that are increasingly being taken over by polymeric materials. It, therefore, appeared logical to extend our exploratory work to a study of the effects of LMP irradiation on the dielectric properties of mica-filled systems based on PE and PS. In particular, it was felt that the Maxwell-Wagner interfacial polarization effect, to be discussed in greater detail below, should reflect sensitively attempts to control the properties of the polymer-filler interface by the plasma treatment. The present paper complements part I by reporting on the dielectric properties of polymeric composites containing irradiated mica.

THEORY OF INTERFACIAL POLARIZATION

A well-known phenomenon in the theory of heterogeneous dielectrics is the interfacial polarization, or so-called Maxwell-Wagner effect. This polarization is generally interpreted as being due to the migration of charge carriers to the boundaries between components of the heterogeneous system, under the effect of an applied (time-varying) electric field. The dielectric behavior of heterogeneous dielectrics has recently been the subject of an excellent review article.³

A composite consisting of parallel layers of two dielectrics of differing electrical conductivities⁴ or, more generally, of spheroids of one dielectric medium embedded in another^{5,6} has been shown theoretically to lead to a Debye-like dispersion spectrum, as is illustrated in Figure 1 (see, for example, ref. 7, p. 228).

In mathematical terms, the real and imaginary parts of the complex relative permittivity $K^*(\omega)$, $K'(\omega)$, and $K''(\omega)$ can be expressed by the well-known Debye equations:

$$K'(\omega) = K_{\infty}' + \frac{K_s' - K_{\infty}'}{1 + \omega^2\tau^2} \quad (1)$$

$$K''(\omega) = \frac{(K_s' - K_{\infty}')\omega\tau}{1 + \omega^2\tau^2} \quad (2)$$

where K_s' and K_{∞}' are, respectively, the low-frequency (or static) and the high-frequency (optical) values of the relative dielectric constant $K'(\omega)$.

When discussing dielectric losses, it is convenient to refer either to the relative loss factor $K''(\omega)$ or to the ratio

$$K''(\omega)/K'(\omega) \equiv \tan \delta \quad (3)$$

In the following, we shall be using both terminologies. $K''(\omega)$ has a maximum value given by

$$K_m'' = \frac{1}{2}(K_s' - K_{\infty}') \quad (4)$$

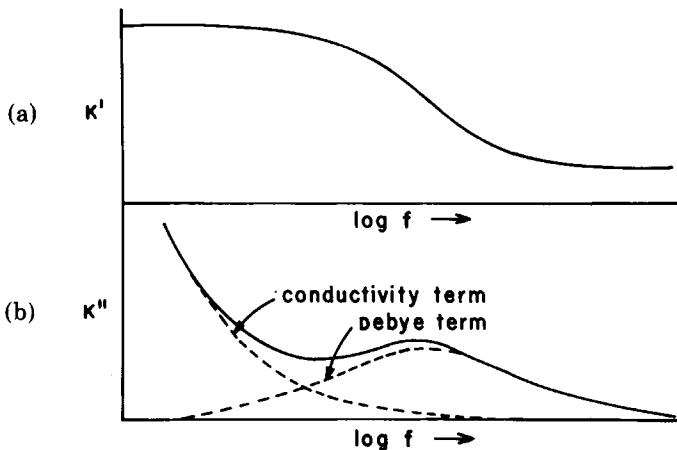


Fig. 1. Relaxation spectrum of an "ideal" Maxwell-Wagner dielectric. (a) and (b) are, respectively, plots of K' and K'' vs. log frequency.

at a frequency f_m which is related to a characteristic time (or relaxation time) τ by

$$\tau = \frac{1}{2\pi} f_m = 1/\omega_m \tag{5}$$

In any case of relaxation in which an appreciable d.c. conductivity σ also exists, the measured loss factor will include an additional term $\sigma/\epsilon_0\omega$, where ϵ_0 is the permittivity of free space. Thus,

$$K''(\omega) = \frac{\sigma}{\epsilon_0\omega} + \frac{(K_s' - K_\infty')\omega\tau}{1 + \omega^2\tau^2} \tag{6}$$

as shown in Figure 1b.

The relative dielectric constant $K'(\omega)$ (Fig. 1a) drops from its static value K_s' to its optical value K_∞' within a frequency range centered at f_m .

It is quite rare for a dielectric to display ideal Debye behavior. Far more commonly, the dispersive frequency range is much broader, in which case one may consider a superposition of relaxation processes to occur, each one characterized by a relaxation time τ . With this "spectrum" of relaxation times is associated a distribution function $G(\tau)$, and eqs. (1) and (2) then become

$$K'(\omega) = K_\infty' + (K_s' - K_\infty') \int_0^\infty \frac{G(\tau)d\tau}{1 + \omega^2\tau^2} \tag{7}$$

$$K''(\omega) = (K_s' - K_\infty') \int_0^\infty \frac{G(\tau)\omega\tau d\tau}{1 + \omega^2\tau^2} \tag{8}$$

As mentioned above, Sillars⁶ treated the most general case of spheroidal particles (medium 2) of permittivity K_2' and conductivity σ_2 , dispersed in a homogeneous dielectric (medium 1) characterized by K_1' , σ_1 , where $\sigma_1 \ll \sigma_2$. Sillars found the following expressions for τ , K_s' , and K_∞' :

$$\tau = \epsilon_0 \frac{K_1' + A_a(1 - V_2)(K_2' - K_1')}{\sigma_1 + A_a(1 - V_2)(\sigma_2 - \sigma_1)} \tag{9}$$

$$K_s' = K_1' \frac{\sigma_1 + [A_a(1 - V_2) + V_2](\sigma_2 - \sigma_1)}{\sigma_1 + A_a(1 - V_2)(\sigma_2 - \sigma_1)} + V_2\sigma_1 \frac{[\sigma_1 + A_a(\sigma_2 - \sigma_1)](K_2' - K_1') - [K_1' + A_a(K_2' - K_1')](\sigma_2 - \sigma_1)}{[\sigma_1 + A_a(1 - V_2)(\sigma_2 - \sigma_1)]^2} \tag{10}$$

$$K_\infty' = K_1' \frac{K_1' + [A_a(1 - V_2) + V_2](K_2' - K_1')}{K_1' + A_a(1 - V_2)(K_2' - K_1')} \tag{11}$$

where V_2 is the volume fraction of the dispersed medium; A_a , the depolarizing factor along the a axis, is given by

$$A_a = \frac{-1}{r^2 - 1} + \frac{r}{(r^2 - 1)^{3/2}} \ln [r + (r^2 - 1)^{1/2}] \tag{12}$$

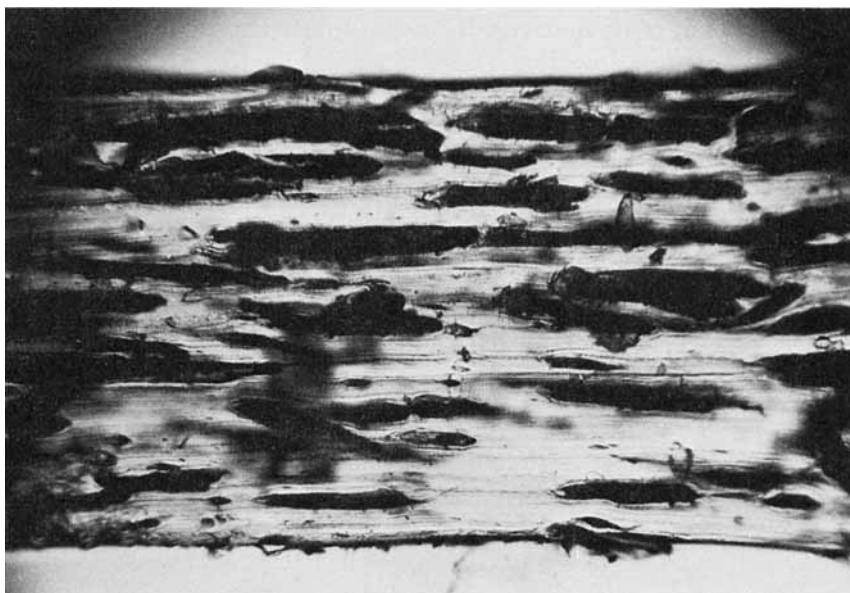
where $r = a/b$, the axial ratio. Equation (12) applies for $a < b$, that is, for the case of oblate spheroids.

In the present study, we are dealing with mica platelets of low axial ratio ($a/b \ll 1$) which are aligned in such a way that their major axis is perpendicular to the direction of the applied electric field. In other words, as the major-



(a)

500 μ



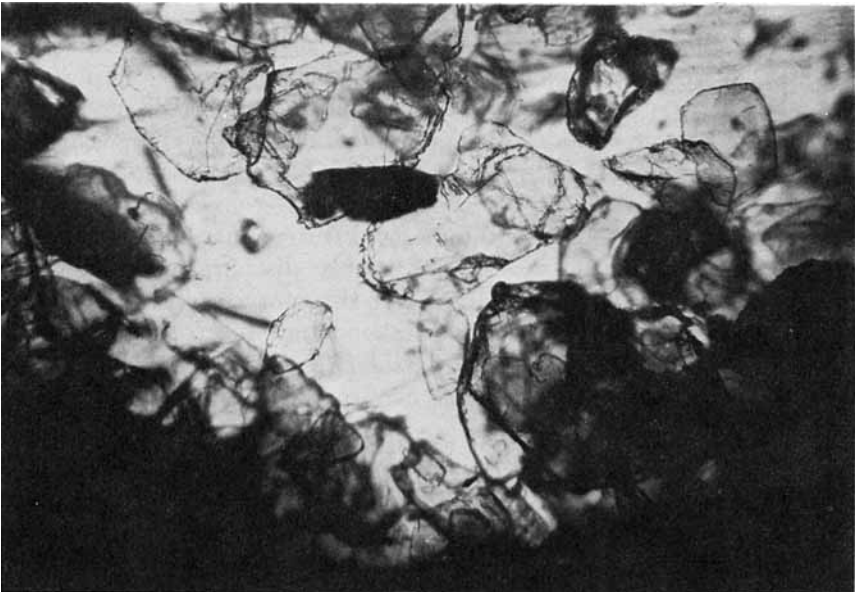
(b)

Fig. 2. Photomicrographs of PE + 10 wt-% mica samples: transverse sectional views of compression-molded plates. The dark, oblong shapes are mica flakes: (a) Brabendered sample; (b) sample produced from "Microthene" powder.



(a)

500 μ



(b)

Fig. 3. Same samples as in Fig. 2, viewed in the plane of the plates.

ity of the mica flakes are oriented during the compression molding process, their plane is parallel to the plane of the disc sample used for the dielectric measurements. Figures 2a and 2b are cross-sectional photomicrographs of PE + 10% mica, showing, respectively, a Brabendered sample and a sample compression molded from PE powder. The average axial ratios, determined microscopically from a large number of flakes, are, respectively, 0.067 and 0.074.

For comparison, Figures 3a and 3b are photomicrographs of the same samples in the plane of the disc. Judging from these photomicrographs, it appears reasonable to simulate the mica flakes by oblate spheroids of the appropriate axial ratios. If we accept this assumption, Sillars' model dielectric can represent the present composite materials, and we can attempt to compare experimental dielectric properties with the theoretical results.

Rather than using the complicated general expressions (10) and (11), the following simpler approximate expressions,³ which apply to the present system, will be used for this purpose (see Discussion):

$$K_s' \simeq K_1' \left[1 + \frac{V_2}{A_a(1 - V_2)} \right] \quad (13)$$

and

$$K_\infty' \simeq K_1' \left[1 + V_2 \frac{(K_2' - K_1')}{[K_1' + A_a(K_2' - K_1')]} \right]. \quad (14)$$

Several authors^{8,9} have pointed out that the Maxwell-Wagner-Sillars (MWS) theory, being purely macroscopic in nature, neglects certain important microscopic effects associated with charge carriers in real systems. Both Trukhan's⁸ as well as Goffaux's⁹ calculations demonstrate the importance of space charge effects; according to the former author, the MWS model applies only when the system contains high concentrations of free charge carriers or, in other words, when the Debye shielding radius is small compared with the dimensions of the system.

Goffaux,⁹ on the other hand, allows for diffusive charge transport within the dielectric media and, by means of a variable "discharge parameter" ρ , calculates the effect of charge transfer across their interfaces. The dispersion relations emerging from this microscopic model are much more complicated than the Debye relations (1) and (2), particularly at low frequencies ($\omega\tau \ll 1$). In this frequency domain, free charge carriers give rise to an additional loss mechanism which has the form

$$K'' = C\omega^{-1/2} \quad (15)$$

C being a constant. There is also a contribution to K' due to the presence of space charges.

These results are not unexpected, for at very low frequency the diffusive range of free carriers during the course of one half-cycle greatly exceeds the width of the space charge region. At high frequencies ($\omega\tau \gg 1$), on the other hand, the contribution of the diffusion mechanism to the dielectric dispersion becomes negligible.

EXPERIMENTAL

Most of the details regarding irradiation procedures, composite preparation, etc., have been adequately described in part I and need consequently not be repeated here. It is, however, useful to recall that samples destined for dielectric measurements were prepared by two distinct methods:

a. In the case of material mixed in the Brabender Plasticorder, small (~ 0.2 cm) crumbs were compression molded at 200°C and 20,000 psi into 3-in. \times 3-in. \times $\frac{1}{8}$ -in. plates from which disc samples (1- to 2-in. diameter, depending upon the electrode system used) were then cut.

b. In some instances, sample plates were compression molded using a well-homogenized mixture of mica flake and PE powder (U.S.I. Microthene). This latter procedure has the advantage of maintaining the initial low axial ratio and uniform size distribution of the mica flakes, that is, of preventing their breakdown in the high shear fields encountered during the Brabendering operation. The reduction in particle size and axial ratio under similar conditions has been studied by Okuno and Woodhams,¹⁰ and is also well illustrated by the photomicrographs in Figures 2 and 3.

In order to avoid moisture adsorption on the sample surface which is capable of greatly affecting loss factor measurements, samples were conditioned prior to measurements using the procedure outlined by ASTM Code No. D-1371.

Measurements of the complex permittivity $K^*(\omega)$ of the sample materials were carried out in the frequency range between 10^{-2} Hz and approximately 20 MHz using three instruments. Between 10^{-2} and 10 Hz, a Harris bridge was used which has been described elsewhere^{11,12} (this instrument was made available to us through the courtesy of Dr. H. St-Onge, Hydro Quebec Institute of Research).

Over the remaining frequency range, two commercial instruments were used; a General Radio 1615A ratio-arm transformer bridge between 50 Hz and 20 kHz, and a Hewlett-Packard 4342A Q-meter (resonant circuit) between 20 kHz and 20 MHz. The sample holders used were either of two-terminal (Rutherford Research, Model 1592) or three-terminal configuration (Keithley Instruments, Model 6105). The measuring techniques have been well described in the literature (see, for example, W. Vaughan in ref. 13) and need no further elaboration here.

Finally, the dc conductivity of the Suzorite mica was measured using a Keithley Model 610C electrometer. For this purpose, silver electrodes were painted onto the largest (~ 1 cm) flakes available. The results of these measurements, part of a wider study of electrical properties of mica, will be the subject of a separate communication.¹⁴

RESULTS

Figures 4a, 4b, and 4c are, respectively, plots of K' , $\log K''$, and $\tan \delta$ versus $\log f$ for a series of five PE-mica composite samples containing between 0 and 50% by weight of Suzorite mica flake. The samples of this series were fabricated by compression molding homogeneous mixtures of PE powder and mica flake (see preceding section). As the main purpose of this series was to es-

establish the basic dielectric behavior of the polymer-mica composites, the sole treatment given the mica was to dry it under vacuum at approximately 100°C.

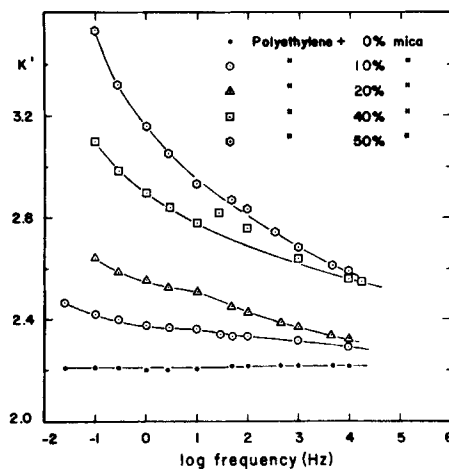
Figures 5, 6, and 7 show permittivity data for the PE-mica, PS-mica, and 0.5 PE + 0.5 PS-mica systems, respectively. In each figure, part a is a plot of K' versus $\log f$, while in part b $\log K''$ is plotted against $\log f$. In order to illustrate the effect of surface treatment of the filler as clearly as possible, only four samples have been represented in each of the figures: the base polymer alone and with 10 wt-% dried mica, and samples in which the mica (10 wt-%) had received a short (90 sec) and long (600 sec) treatment in an ethylene plasma.

All four figures are seen to display the same general behavior: K' of the pure matrix polymer is constant over the entire frequency range studied, whereas, for the composite samples, it has a plateau at high frequencies ($f > 10^5$ Hz) and rises monotonically with decreasing frequency. The numerical values of K' for the pure matrix polymers ($2.2 \leq K' \leq 2.3$ for PE, $K' \approx 2.5$ for PS) and their independence of frequency agree well with published data⁷ and may be considered an internal check on the experimental procedure and the quality of the results.

For the pure matrix polymers, K'' (or $\tan \delta$) have low and nearly constant values at low frequency, but rise slightly at high frequency ($\geq 10^4$ Hz). At 1 kHz, for example, $\tan \delta \leq 5 \times 10^{-4}$ in all cases. Again, this numerical result and the observed frequency dependence are in agreement with published data.⁷

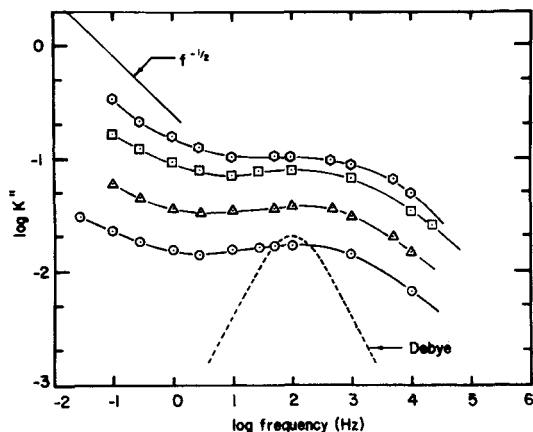
In the case of the composite materials, however, K'' is at least an order of magnitude greater than that of the pure matrix, at low frequencies. At high frequency, K'' generally drops off and approaches the matrix value.

Figures 5 to 7 show that surface treatment of the mica can significantly influence the dielectric behavior of the composite materials. Although there

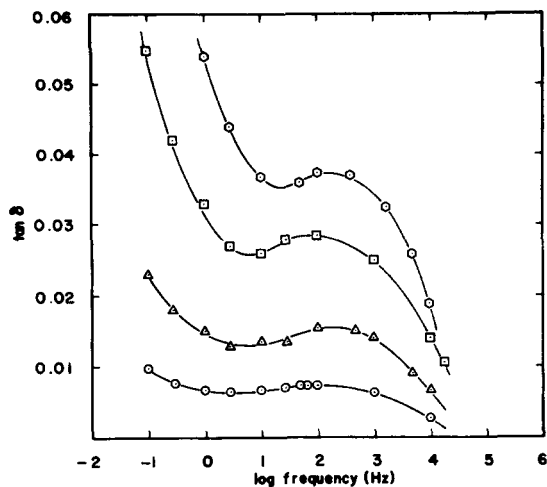


(a)

Fig. 4 (continued)



(b)

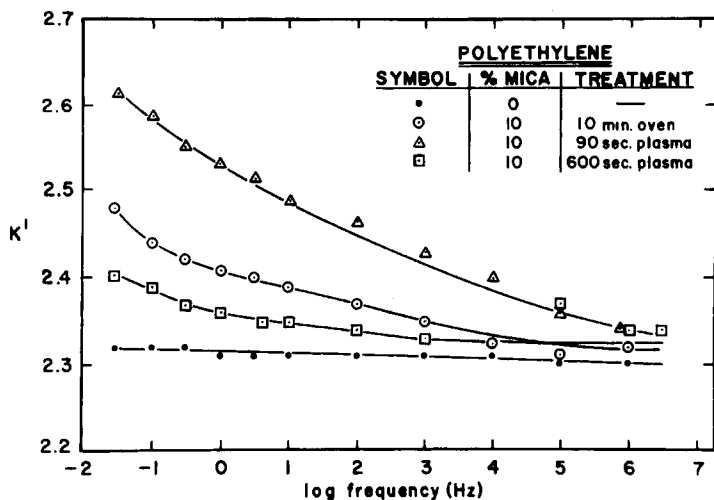


(c)

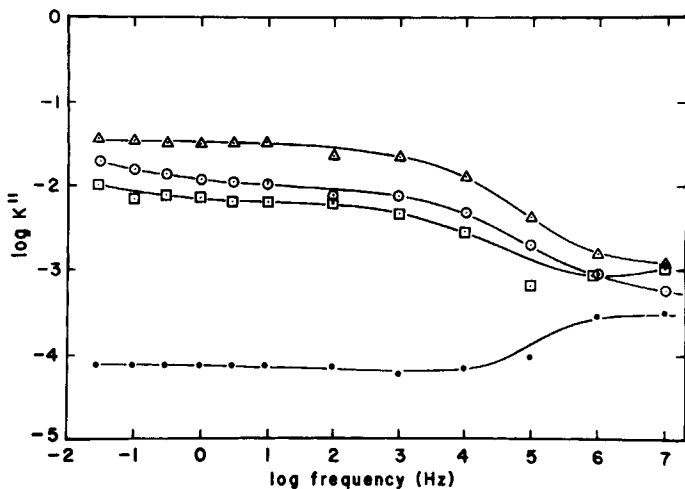
Fig. 4. (a), (b) and (c) are, respectively, plots of K' , $\log K''$ and $\tan \delta$ versus log frequency for a series of PE-mica composites (compression molded from "Microthene" powder) containing 0 to 50% by weight of oven-dried mica flake.

are several features which are common to the three polymer systems studied, details of the variation of K^* with frequency and with surface treatment differ from one system to the other. A qualitative discussion of these results is given in the discussion section.

In an attempt to distinguish between surface treatment effects on the one hand and the intrinsic dielectric properties on the other, it was felt important to study the latter in the series of "ideal" composites (Fig. 4), that is, in materials which approach the theoretical MWS model as closely as possible. A comparison between theory and experimentally observed behavior of the "ideal" materials is given in the following section.



(a)



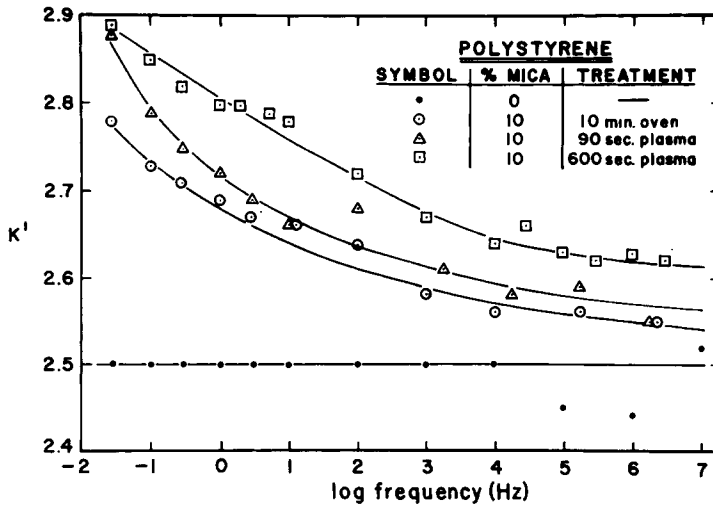
(b)

Fig. 5. Plots of K' (a) and $\log K''$ (b) vs. \log frequency for the PE-mica system (zero and 10 wt-% mica). Surface treatment of the mica prior to composite fabrication is indicated, see legend.

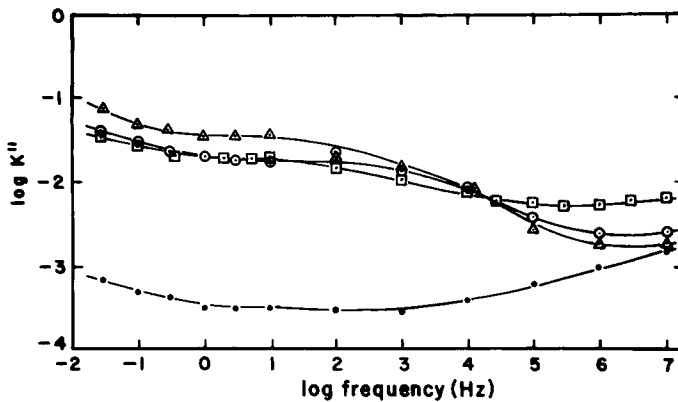
DISCUSSION

Comparison with the MWS Model

Dielectric loss of every type is connected with the motion of charge carriers; as all the matrix polymers used in this study are nonpolar (that is, they do not contain molecular groups with permanent electric dipole moments), the only loss mechanism active in the case of the pure polymer samples is the so-called electronic polarization (due to relative displacement of electrons and nuclei); hence the low losses and flat frequency responses noted in Figures 4 to 7.



(a)



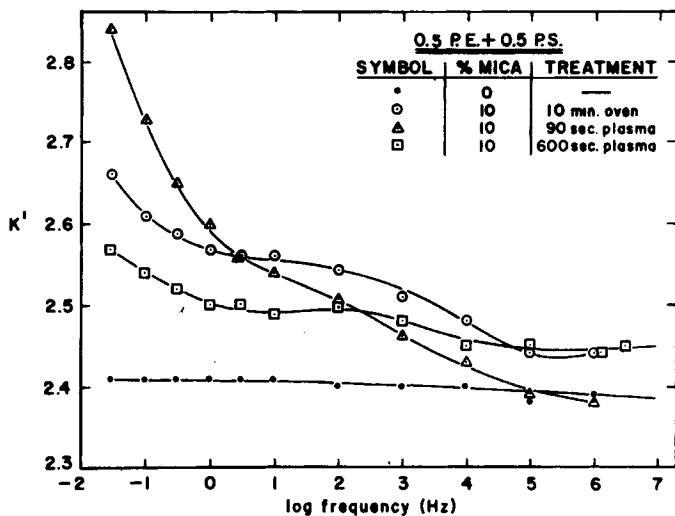
(b)

Fig. 6. Plots of K' (a) and $\log K''$ (b) vs. \log frequency for the PS-mica system.

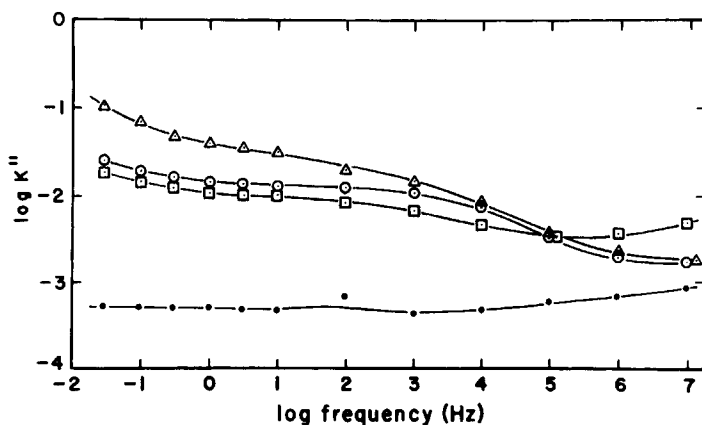
When mica flakes are added, however, an additional loss mechanism, the interfacial polarization or Maxwell-Wagner effect discussed in the section on the theory of interfacial polarization is present. This is manifested by the sharp rise in losses of the composite materials shown in Figures 4 to 7.

At this point, we present a semiquantitative comparison between experimental results for the series of "ideal" samples (Fig. 4) and the MWS theory outlined above. The MWS theory predicts a Debye-like dispersion spectrum having characteristic parameters K_s' , K_∞' , K_m'' , and τ given, for the present geometry, by eqs. (13), (14), (4), and (9), respectively. Inspecting Figure 4b, we indeed note peaks in K'' near $f_m = 100$ Hz, which are augmented at low frequencies by a monotonically rising, additional loss term. Inspecting the lowest frequency data available, this term appears to be of the form

$$K'' \approx Cf^{-x} \quad (0.23 \lesssim x \lesssim 0.43) \quad (16)$$



(a)



(b)

Fig. 7. Plots of K' (a) and $\log K''$ (b) vs. log frequency for the system 0.5 PE plus 0.5 PS-mica.

where C is a constant. This is reminiscent of Goffaux's⁹ low frequency loss given by eq. (15); in fact, noting that for all four curves shown in Figure 4b the slope (x) is still increasing at the lowest frequency measured, it is suggested that the charge diffusion mechanism proposed by Goffaux⁹ is responsible for the observed low frequency losses. There are other reports in the literature¹⁵ according to which losses of the type given by eq. (15) have been observed in heterogeneous systems.

If we accept the preceding arguments according to which K'' is composed of a "diffusive" and a "Debye" term, we can proceed to analyze the latter contribution to the overall dispersion spectrum. In Table I, we have summarized characteristics of the two dielectric media required for the numerical evaluations.

TABLE I
Characteristics of the Two Dielectric Media Comprising the Composite Materials

	Polyethylene (medium 1)	"Suzorite" mica (medium 2)	Remarks
K'	2.21	5.70	
$\sigma, (\Omega\text{-m})^{-1}$	$\sim 10^{-17}$	$\sim 10^{-10}$	ref. (12)
A_a		0.90	for $a/b = 0.070$

In Table II, the calculated data are summarized, together with corresponding experimental results.

Comparing theoretical and experimental values of K_m'' or $(\tan \delta)_m$, satisfactory agreement is noted, especially for low mica concentrations ($V_2 \ll 1$), where the theoretical formulæ used are particularly good approximations.

On the other hand, the agreement is less satisfactory in two respects: First, although theory predicts a very weak dependence of τ upon V_2 , in accord with experimental observation, its numerical value is roughly two orders of magnitude larger than the experimental relaxation time. No satisfactory explanation for this discrepancy can be offered at the present time. Secondly, the observed peak is substantially broader than the Debye peak; for comparison, the latter has been shown by the dotted curve in Figure 4b for the case of 10% mica. In the theory section, we have indicated that such a broadening is symptomatic of a spectrum of relaxation times, characterized by a distribution function $G(\tau)$. This interpretation is compatible with our observation (see Table II) that the theoretical value of K_m'' always exceeds its experimental counterpart.⁷

With reference to eq. (9), from which τ is seen to depend upon A_a , the present distribution of relaxation times might be explained qualitatively as follows: As shown in Figures 2b and 3b, the mica flakes are not identical but have sizes and shapes distributed around a certain average value. Each of these different "spheroids," having a slightly different value of A_a , will give rise to a different τ . Furthermore, and probably more important, some of the flakes are not oriented perpendicular to the direction of the electric field, and this has the effect of changing not only A_a but also K_2' and σ_2 in eq. (9), as mica is highly anisotropic.¹⁴ It is also conceivable that additional mechanisms such as those postulated by Garton¹⁶ and more recently by Jonscher¹⁷ may be contributing to the observed broadening of the loss peak.

Turning now to K' , we may note additional experimental support for the MWS theory: In Table II, good agreement is seen to exist between calculat-

TABLE II
Comparison of Calculated and Corresponding Experimental Results
for the "Ideal" Sample Series

Mica, wt-%	V_2	K_s'		K_∞'		$K_m'' \times 10^2$		$(\tan \delta)_m \times 10^2$		τ, sec	
		Theory eq. (13)	Theory eq. (14)	Expt. (10 kHz)	Theory eq. (4)	Expt.	Theory eq. (3)	Expt.	Theory eq. (9)	Expt.	
10	0.0365	2.303	2.263	2.29	2.00	1.70	0.86	0.73	0.53	1.6×10^{-3}	
20	0.0785	2.419	2.323	2.32	4.80	3.70	1.98	1.50	—	—	
40	0.1851	2.768	2.477	2.56	14.55	8.20	5.27	2.85	—	—	
50	0.2541	3.047	2.576	2.59	23.55	10.50	8.29	3.75	0.60	1.6×10^{-3}	

ed and experimental (10 kHz) values of K_{∞}' , even for the higher mica concentrations. (The comparison is justified since, referring to Figs. 5 to 7, K' varies only little ($\sim 2\%$) between 10^4 Hz and the highest frequencies at which measurements were carried out.) It is not possible to compare theoretical and experimental values of K_s' since the latter are obscured by the space charge contributions⁹ (see theory section) to K' .

Effects of Surface Treatment

Having established the main features of the dielectric dispersion behavior, we may now consider the effects of surface treatments, as illustrated by Figures 5 to 7.

As a general comment, it should be pointed out that dielectric permittivity measurements have proved to be a very sensitive index of sample quality. For example, in some preliminary work, porosity due to the presence of small air bubbles was inadvertently introduced during the fabrication process, resulting in an appreciable lowering of K' ; when these materials were repressed in order to eliminate their porosity, K' was raised to the "ideal" value. Similarly, inspecting Figures 5 to 7, dielectric spectra show up apparent variations in sample characteristics which would be very difficult to detect by other techniques.

Figures 5 to 7 display the same important features described in the discussion of the MWS model above, with the possible exception that the "Debye" contribution to K'' appears to be even broader than for the "ideal" sample series of Figure 4. As we are dealing with Brabendered materials in this section, this additional broadening is presumably related to the wider variety of "ellipsoid" geometries and orientations found in these sample materials (see Figs. 2a and 3a). The low frequency plateau in the Debye spectrum of K' , which we were unable to detect in Figure 4 on account of the space charge term,⁹ is quite apparent in the PE + PS system (Fig. 7a).

Closer inspection of the loss spectra reveals that Figures 6b and 7b are strikingly similar among themselves, but differ appreciably from Figure 5b; in particular, K'' for the PE system is generally lower at high ($\geq 10^5$ Hz) and low (≤ 1 Hz) frequencies. It also appears significant that the sample material having the lowest overall losses is the PE composite containing 600-sec-treated mica. These features suggest that mica treatment in an ethylene plasma has a more favorable effect on PE composites than on PS and PE-PS composites, a result which agrees well with rheological and mechanical results described in part I.

There are several characteristics displayed by the three composite systems upon which we can only speculate at the present time. For example, all three loss spectra show that increasing plasma treatment time produces first a rise, then a drop in K'' , the 600-sec curves lying below the oven-dried curves in all cases, except at high frequencies ($\geq 10^5$ Hz) where the 600-sec loss curve is substantially higher and tends to rise further with increasing frequency.

Differences between plasma-treated and untreated composites can also be noted in the K' spectra, although here the effect of plasma treatment time is less evident.

It appears certain from the foregoing that surface modification of the mica filler by plasma irradiation has a substantial influence upon the dispersion characteristics of a given composite material over the entire frequency range investigated. In an attempt to explain the observed effects at the present time, we can only offer some speculative suggestions. If we accept that treatment of the mica flakes in an ethylene plasma results in the deposit of a thin, highly crosslinked "polyethylene" layer having electrical properties presumably quite different from those of both the mica and the matrix polymer, then the resulting composite materials must be considered to contain three distinct dielectrics. Judging from the complexities of the theories of binary systems,^{6,9} even the most simplistic theoretical analysis of such a ternary composite offers a major challenge.

Here, we merely emphasize that theoretical treatments such as those of Goffaux⁹ and Trukhan⁸ would lead one, *a priori*, to expect significant contributions to the dispersion spectra, at least at low frequencies, even if the coating on the mica particles is very thin indeed. Besides the present data, there is other evidence in the literature that very thin surface coatings can have pronounced effects upon K^* , even at intermediate frequencies.¹⁸

To conclude this section, it is appropriate to note two points connected with the practical aspects of plasma treatment. First, if composite polymers of this type were considered as candidates for insulating materials in power frequency (60 Hz) applications, plasma treatment of the filler would evidently be advantageous, for K'' is seen to drop by a factor of 2 (for the 600-sec curves) compared with the untreated material. Secondly, as has already been underlined in part I, no attempt has yet been made to optimize the plasma treatment conditions. Consequently, similar or even greater beneficial effects than those illustrated here may be achievable by "optimized" plasma treatment of much shorter duration,¹⁹ a point evidently of great pertinence to possible practical application. Present studies are directed toward determining those "optimum" plasma treatment conditions.

CONCLUSIONS

We have examined the dispersion behavior of the complex relative permittivity $K^*(\omega)$ of polymer-mica composites (10 wt-% mica) over a wide frequency range extending from about 10^{-2} Hz to above 10^7 Hz. Microwave plasma treatment in ethylene of the mica flakes leads to significant alterations of $K^*(\omega)$ compared with untreated mica for all three matrix polymers investigated—PE, PS, and 0.5 PE + 0.5 PS. For example, the dielectric loss factor K'' can be reduced significantly over most of the frequency range, including power frequency (60 Hz). No attempts have yet been made to optimize the plasma treatments from the point of view of possible future practical applications.

The origins of the dispersion characteristics have been investigated using a series of "ideal" samples containing 10, 20, 40, and 50 wt-% untreated mica in a PE matrix. Comparing the experimental results with theoretical analyses of the interfacial polarization (Maxwell-Wagner) effect by Sillars⁶ and Gof-

faux,⁹ it is possible to identify a broad, Debye-like peak in K'' , located in the audio frequency range. At low frequency, an additional term of the type

$$K'' = Cf^{-x} \quad (x \simeq 0.5)$$

owing to a charge diffusion mechanism⁹ contributes to the loss spectrum.

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