Dielectric properties of moist $CaCO_3$ filled polyethylene composites

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Abstract: The capacitance and the dielectric loss tangents of $CaCO_3$ filled polyethylene composites were studied. Composite samples, prepared by polymerizing ethylene on the surfaces of fillers, pre-treated by polymerization catalysts, were compared to normal mechanical mixtures. Dielectric dispersion, ε', and loss, ε'', proved to be sensitive to heating or vacuum treatment. Investigation of samples under conditions of different relative humidities showed that the dielectric dispersion is due to adsorbed water. Both ε' and ε'' increased with decreasing frequency and the ratio of loss and dispersion was nearly constant. Dielectric data measured at different relative humidities could be represented by a single Cole-Cole plot. Samples soaked in water for different periods yielded qualitatively similar but quantitatively different Cole-Cole plots. Composite samples showed higher losses at similar humidities.

Possible interpretations in terms of a molecular relaxation model, an interfacial relaxation model, including a charged double layer mechanism, percolation theory and the universal response theory were examined, but none was able to fully explain the observed phenomena.

Key words: Dielectric properties, composites, humidity effect, interfacial polarization.

Introduction

Preliminary studies on the dielectric properties of polyethylene-calcium carbonate composites have been described in a previous publication [1]. It was established that samples stored under ambient conditions exhibit dielectric loss which disappears on heating or vacuum treatment. This phenomenon has been attributed to adsorption of atmospheric water on to the filler-polymer interface. In continuing this work further dielectric measurements have been performed on samples quantitatively exposed to water and water vapor.

The main purpose of these investigations was to determine the relationship between water content and dielectric properties and to obtain further information about the nature of the relaxation process.

Experimental

Materials

The composite samples were kindly provided by Dr. E. G. Howard (DuPont de Nemours). These composites were prepared by a special method: the filler particles were surface treated by a polymerization catalyst; subsequently ethylene gas was polymerized onto the surface of the filler [2]. Composites of this type are denoted "homogeneous" because even at high filler content (50–70 wt %) there is strong adhesion between the matrix and the filler; agglomeration of filler particles is less pronounced than in conventionally prepared mechanical mixtures. The improved mechanical properties of these composites [3] are believed to be due to a special kind of grafting; the titanium catalyst is covalently bonded to the polymer chains and is ionically bound to the crystal lattice of the filler. Composites containing 48.1 wt % filler, and 62.5 wt % filler were studied. These samples will hereafter be designated as D48 and D62, respectively. Another sample containing 20 wt % filler, designated as D20 (62), was prepared from D62 by mixing with pure polyethylene.

A series of mechanical mixtures was prepared in a conventional manner, for comparison with the above described composites. The polymer component was Hifax-1900 ultra high molecular weight polyethylene (Hercules Powder Co.) [4] and the filler was Atomite Code A (Thompson, Weinman & Co.) surface treated with 0.5 wt % TTS (isopropyl triisostearyl titanate, Kenrich Petrochemicals, Inc.). Samples containing 10–60 wt % filler will be designated as H10–H60. Further details of sample preparation have been described previously [1].

Measurements

The measurements of the capacitance and the loss tangents were performed by a General Radio 1620 assembly with a three terminal Balsbaugh cell. The electrode diameter was 5.5 cm and the sample thickness varied from 0.25 to 0.75 mm. Contact between the electrodes and the sample was obtained by pressing a thin Al foil to the sample surface. Evaporated electrodes are essential in sub-audio frequency measurements, but usually not in the kilohertz range. Evaporated metal layers could influence water vapor diffusion and their surface chemistry could change under the effect of water, so they were omitted. For further details of data processing see Reference [1].

Dielectric samples were maintained in desiccators above various salt solutions [5] for two days, and water adsorption was monitored by measuring changes in weight.

Results

Composite samples obtained from Du Pont, the D series, show a strong dielectric dispersion as a function of temperature up to the melting point of the polyethylene component; this dielectric dispersion disappears on cooling. Figure 1 shows the temperature dependence of the real portion of the complex permittivity, ε', for sample D62 at three different frequencies (curves a). An overnight vacuum treatment of sample D62 at room temperature markedly reduces the frequency dependence of ε' (curve b). Pure polyethylene., Hifax-1900, shows no dispersion; ε' decreases around the melting point (curve c). This decrease is probably due to the density change in the melting-premelting range. The sample was not totally dried by room temperature vacuum treatment as indicated by the continuous decrease of dielectric losses, ε'', upon subsequent cooling (Fig. 2). The same phenomenon is displayed by the mechanical mixtures but in this case both the losses and the frequency dependence of ε' are diminished. Figure 3 shows the temperature dependence of the dielectric loss of sample H40, which had been previously stored under ambient conditions for several days.

To establish the permittivity/filler content relationship for dry samples, the following method was applied. H series samples containing 10, 20, 30, 40, 50 and 60 wt % Atomite filler were heated to 135 °C, dried at this temperature for an hour and subjected to measurements of complex permittivity upon cooling
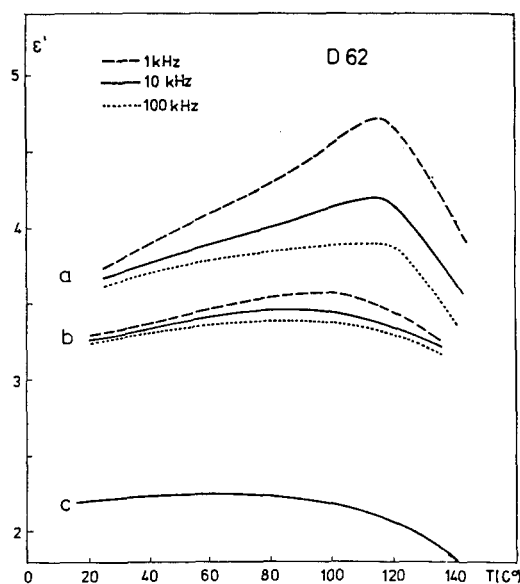

Fig. 1. Dielectric permittivities, ε' of D62 samples (a, b) and pure polyethylene (c). Sample a was stored under ambient conditions and sample b was vacuum treated for 12 hours at room temperature. All curves were recorded during heating
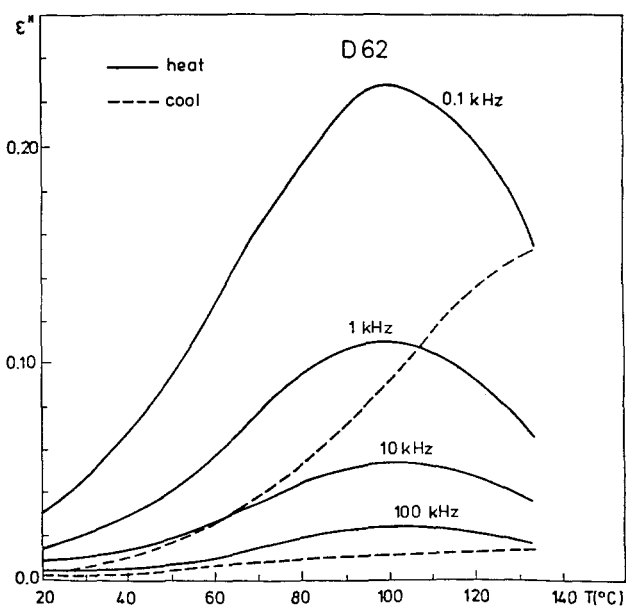

Fig. 2. Dielectric loss, ε'', of a D62 sample upon heating and cooling. The sample was vacuum treated for 12 hours at room temperature before heating
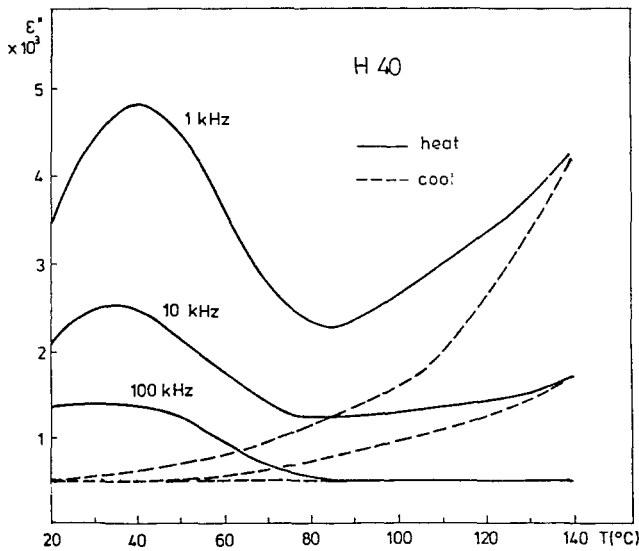
Fig. 3. Dielectric loss, ε'', of a H40 sample stored under ambient conditions upon heating and cooling

under dried N_2 gas. In addition pure Hifax-1900, D48 and D62 samples were also investigated under these conditions. For each case, parallel measurements of three samples were made. The ratio of the 100 kHz composite permittivities to that of the pure Hifax-1900 sample proved to be practically independent of the temperature. (This quantity shows less variation at different temperatures than the parallel samples show at constant temperature.) These ratios with standard
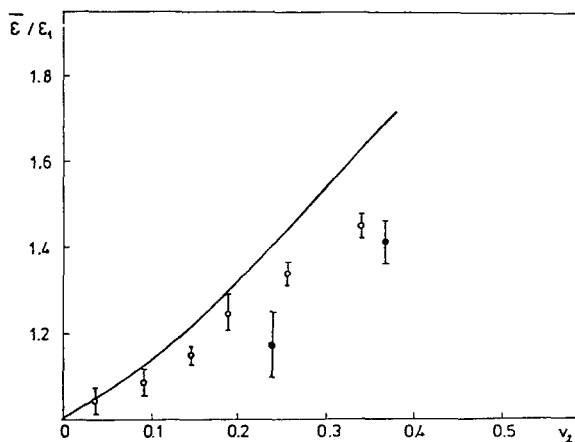

Fig. 4. Ratio of the 100 kHz permittivity of various composites and pure polyethylene as a function of filler volume fraction with standard deviations. H10–H60 samples (○); D48 and D62 (●). Line denotes the calculated curve (see Discussion)
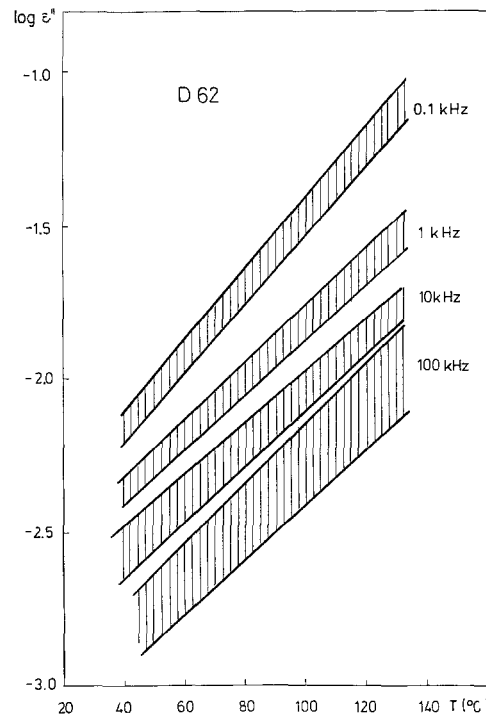

Fig. 5. Residual dielectric loss on cooling for the D62 sample after drying for 1 hour at 125 °C. Data points of three parallel measurements lie within the shaded areas

deviations are shown in Figure 4 as a function of filler volume fraction.

Even after prolonged heating, the material retains some frequency dependent loss which increases with decreasing frequency and with increasing temperature. Figure 5 shows the temperature dependence of these residual losses upon cooling for sample D62. (The shaded areas on this and later figures denote the limits within which the data points lie.) The 10 kHz losses of D62 and D48 upon cooling are compared in Figure 6. As previously observed [1] D48 shows far less dielectric loss than D62. This smaller dielectric loss of D48 cannot be explained solely by the difference in the filler content; it is probably due to a difference in the surface pre-treatment of the materials. To test this hypothesis another sample was prepared from D62 by mixing with Hifax-1900. This sample is denoted as D20(62) as it contains 20 wt % filler. In Figure 6 it can be seen that the loss of D20(62) essentially parallels that of D62. The dielectric loss values for D20(62) themselves are close to those measured for D48 which contains more filler. Residual losses of the mechanical mixtures at 10 kHz are presented in Figure 7. The qua-
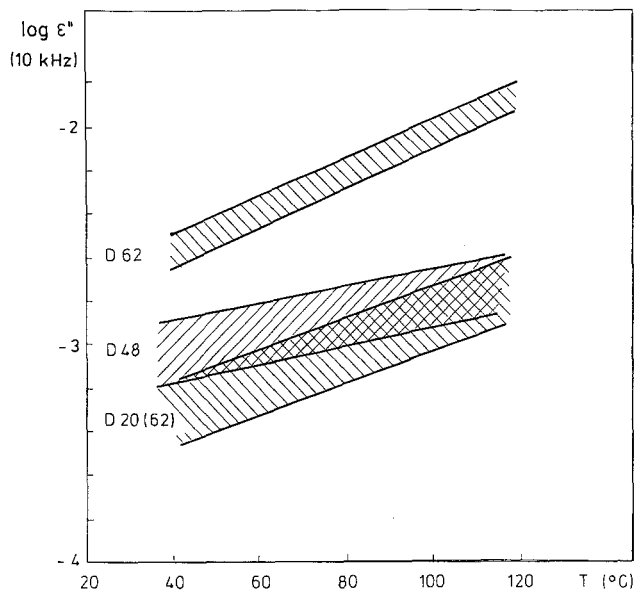
Fig. 6. Residual dielectric losses for cooling in dried D62, D48 and D20(62) samples
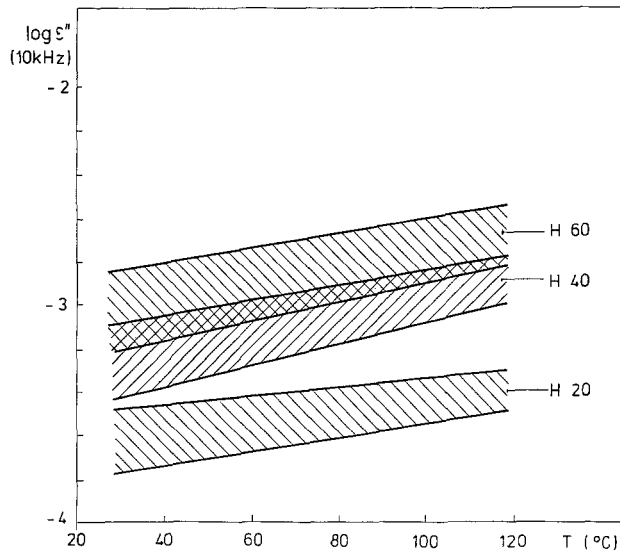
Fig. 7. Residual dielectric losses on cooling for dried samples of the H series

litative behavior of the residual losses is similar to that of the D series composites; however, the loss values are smaller. The loss of H60 is comparable to that of D48 and the dielectric loss decreases systematically with decreasing filler content.

The effect of exposure to humid air on the samples was studied. Most of the measurements were performed using D62, because this sample proved to be most sensitive to water adsorption [1] but D48 and the mechanical mixtures were also studied. The rest of the dielectric measurements were performed at room temperature.

A D62 sample was dried for two days at 80 °C in a vacuum oven; it was then placed in a desiccator above a saturated CaCl₂ solution which maintains 32 % relative humidity [5] and the dielectric loss was measured at different intervals. Figure 8 shows the measured loss as a function of time. It is clear that even for a sample nearly 0.8 mm thick, more than 90 % of the final loss appears within two days and the treatment can be regarded as complete. Therefore, the samples were maintained above various saturated salt solutions for two days.
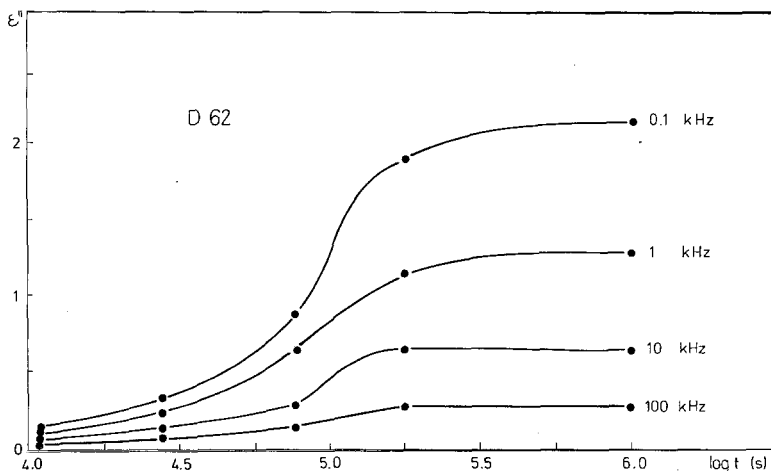
Fig. 8. Dielectric loss as a function of time in a D62 sample exposed to air of 32 % relative humidity
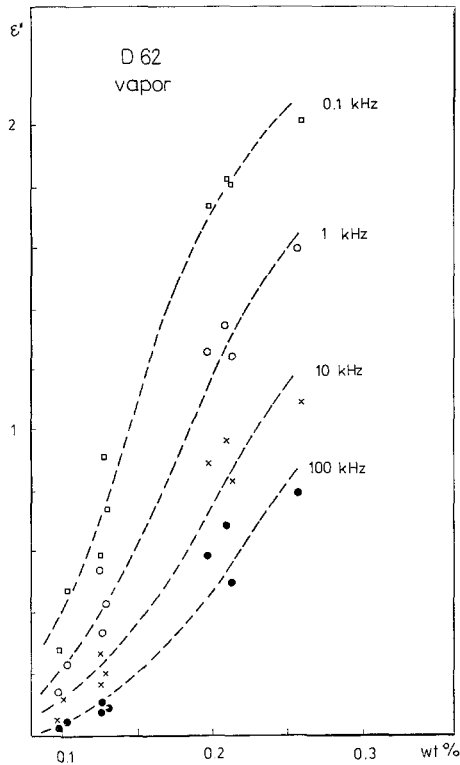
Fig. 9. Dielectric loss of D62 samples exposed to air of different relative humidities as a function of adsorbed water content
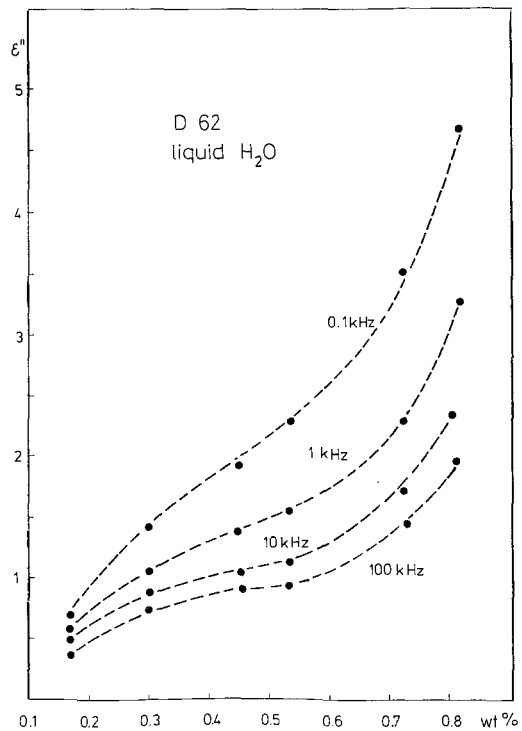

Fig. 10. Dielectric loss of a D62 sample soaked in water for different times as a function of water content

The averages of the dielectric losses are plotted against the adsorbed water content for D62 samples at four different frequencies in Figure 9. Samples were also soaked in liquid water for different periods and the resulting dielectric losses as a function of water content are shown in Figure 10. The Cole-Cole plot of the dielectric data for D62 samples is shown in Figure 11. This figure also includes some points measured for D62 samples soaked in a saturated NaCl solution for differ-
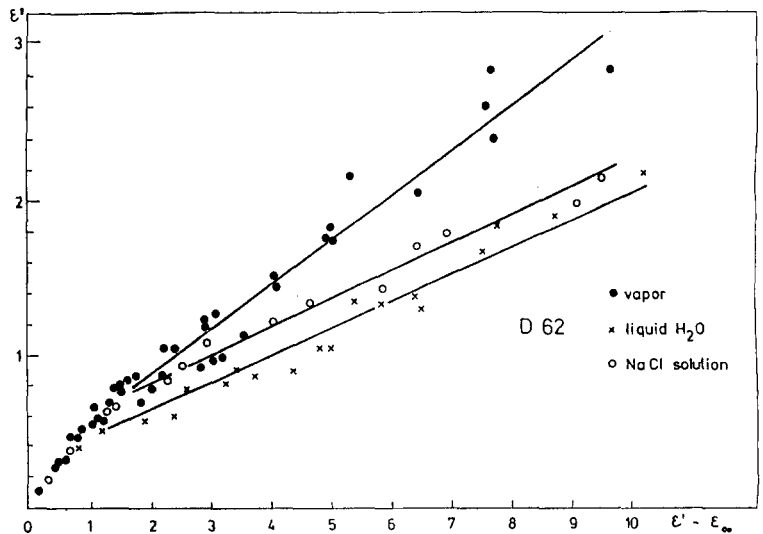

Fig. 11. Cole-Cole plot of the dielectric data for D62 samples exposed to humid air, soaked in water and in NaCl solution. Points corresponding to different relative humidities or to different soaking times can be superposed on a single Cole-Cole plot
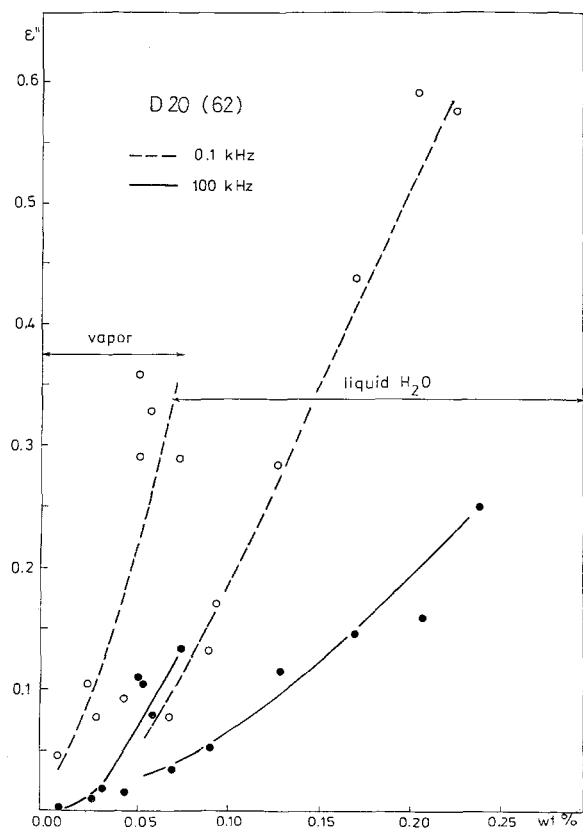
Fig. 12. Dielectric loss in the D20(62) samples exposed to humid air and soaked in water as a function of water content.

ent times. Figures 9 and 10 show that the dielectric loss increases with increasing water content, while Figure 11 indicates that the dielectric permittivity of samples soaked in water increases faster than the loss as compared to vapor-treated samples.

Comparative measurements were performed on D20(62) samples. Dielectric losses as a function of water content are shown in Figure 12. It can be seen in Figures 9 and 12 that both water content and dielectric losses for D20(62) are reduced, compared to those for D62, as expected. One can see in the Cole-Cole representation of these data (Fig. 13) that the curve of the water-soaked samples again lies below that of the vapor-treated samples. In this case, however, the slopes are practically identical at higher losses and are different at low losses.

Dielectric properties of D48 samples proved to be much less sensitive to water adsorption. Only the Cole-Cole plots are presented (Fig. 14) for humid air-treated and water-soaked samples. Maximal water uptake was around 0.1 wt% in humid air and 0.25 wt% in liquid water.

The 10 kHz losses of the H10–H60 series are plotted versus the filler content at four different relative humidities in Figure 15. As with the D series, the amount of adsorbed water for the H series was again of the order of 0.1 wt %, but the resulting losses were much less than those for the D series. The measured
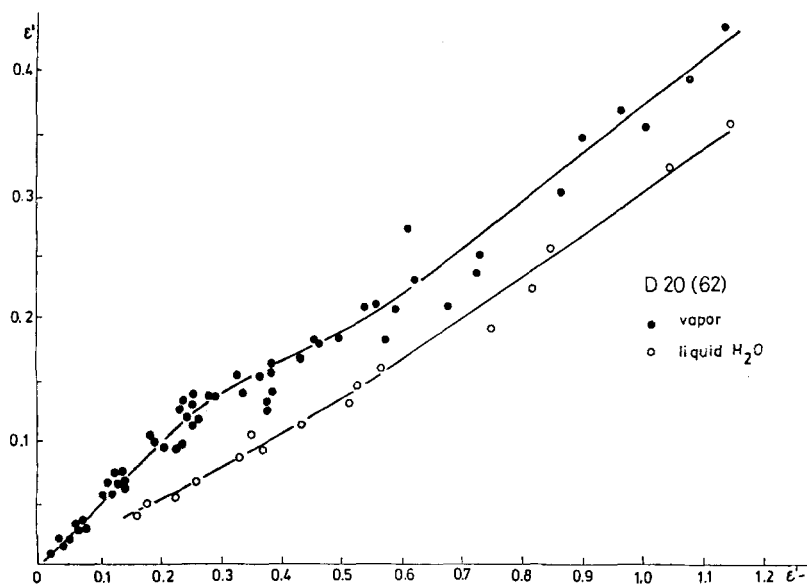

Fig. 13. Cole-Cole representation of the dielectric data measured on D20(62) samples treated in humid air and soaked in water
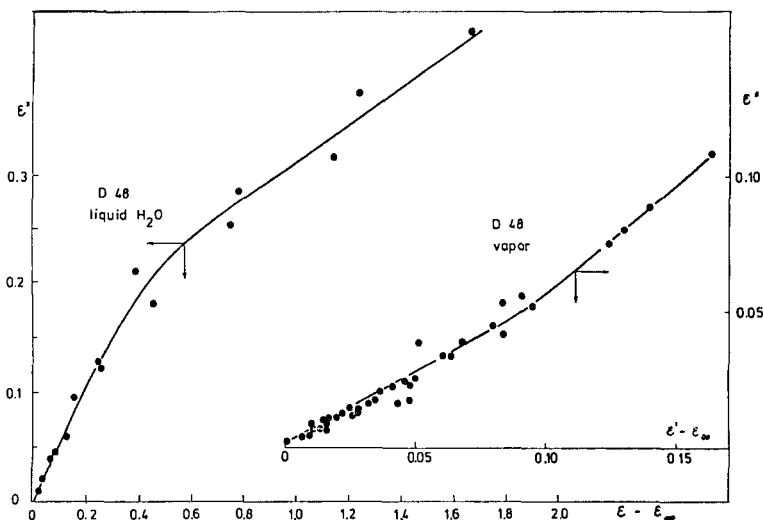
Fig. 14. Cole-Cole representation of the dielectric data measured on D48 samples treated in humid air and soaked in water. (Note, the scales of the ordinates and abscissae in Figures 13 and 14 are different.)

losses increased both with increasing filler content and with relative humidity. Soaking in water did not alter the dielectric properties dramatically. The frequency dependence of dielectric dispersion and loss (i. e. the Cole-Cole plot) is similar to those observed for the D series but on a much smaller scale (Fig. 16).

The most important experimental results can be summarized as follows:

(a) samples exposed to ambient air show increasing dielectric dispersion and loss with decreasing frequency;

(b) both dispersion and loss increase at first and then decrease upon heating;

(c) dielectric dispersion and loss decrease considerably after vacuum or heat treatment, but even after prolonged heating some frequency dependent loss remains;

(d) the loss shows no peak in the range of frequency 10 Hz–100 kHz and the ratio of loss and dispersion is nearly constant over a certain range of frequency and water content;

(e) exposure to humid air or liquid water increases the losses but the qualitative results are the same;

(f) samples soaked in liquid water differ from samples exposed to humid air, even if they contain similar amounts of water, and

(g) dielectric data for the same sample containing different amounts of water can be represented on a single Cole-Cole plot, but the curves of the humid air-treated and water-soaked samples are different, even for the same sample.
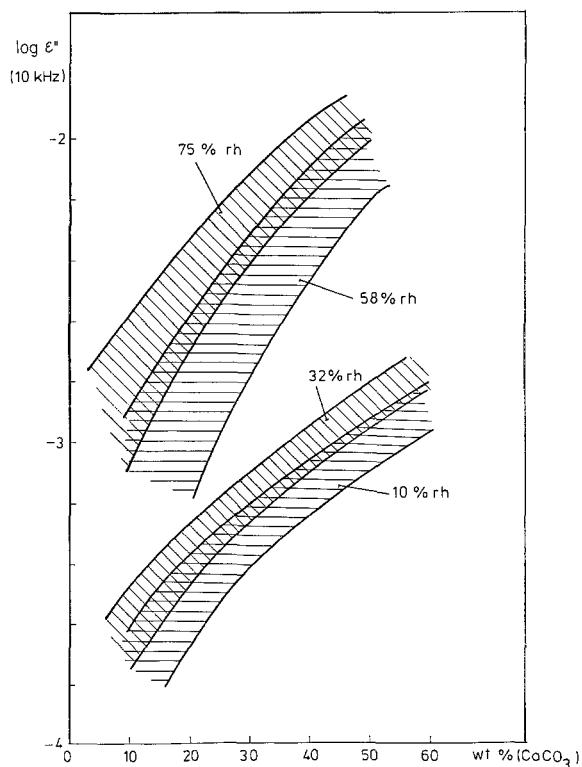

Fig. 15. Dielectric loss in the H series as a function of filler content at four different relative humidities
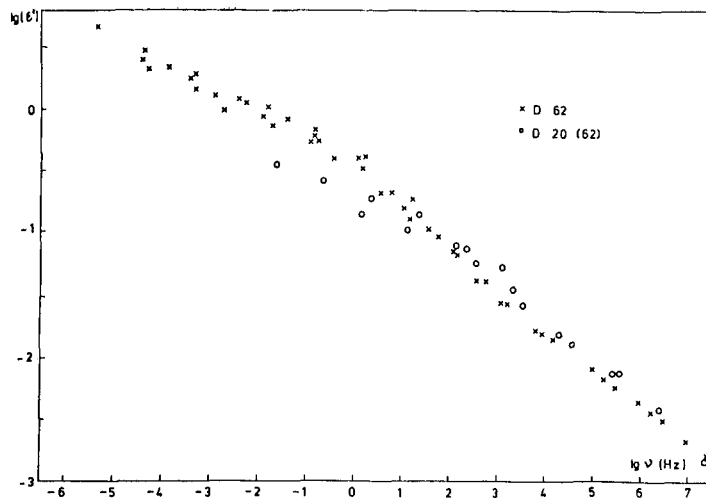
Fig. 16. Superposed master curve of the loss data measured on D62 and D20(62) samples at different relative humidities

Discussion

The dielectric constant for a heterogeneous mixture can be calculated using one of several mixture rules published in the literature [6]. For two component composites containing spherical filler particles, the high frequency composite permittivity $(\bar{\varepsilon})$ can be calculated by using the Bruggeman formula [6]:

$$\left(\frac{\bar{\varepsilon} - \varepsilon_2}{\varepsilon_1 - \varepsilon_2}\right)\left(\frac{\varepsilon_1}{\bar{\varepsilon}}\right)^{1/3} = 1 - v_2 \qquad (1)$$

where ε_1 and ε_2 are the permittivities of the matrix and the filler, respectively, and v_2 is the volume fraction of the filler. This equation reduces to the classical Wagner formula at low filler concentration [6]:

$$\bar{\varepsilon} = \varepsilon_1 \frac{2\,\varepsilon_1\,(1 - v_2) + \varepsilon_2\,(1 + 2v_2)}{\varepsilon_1\,(2 + v_2) + \varepsilon_2\,(1 - v_2)} \qquad (2)$$

To compare the theory with the experimental data, $\bar{\varepsilon}$ was calculated using Equation (1) with $\varepsilon_2 = 8.0$ for CaCO₃ [7] and $\varepsilon_1 = 2.2$ for the polyethylene matrix. ε_2 is taken as the mean value of the dielectric constants of the calcite single crystal [7] while ε_1 is the experimentally obtained value for Hifax-1900: (see also Reference [4]). Since the dielectric constant of polyethylene depends partially on the crystallinity, the value for Hifax-1900 has been chosen to fit the molecular weight of the polyethylene component of the D series samples [1]. It can be seen in Figure 4 that this tendency is reproduced (open circles) but the absolute values are small. (The curve calculated using Equation

(2) was omitted because the difference between Equations (1) and (2) in the volume fraction range indicated is smaller than the standard deviations of the experimental data.) The two D series composites (filled circles) show even lower permittivities. These discrepancies could arise from microvoid formation detected by density measurements in the case of mechanical mixtures [8] or from the lower dielectric constant of the filler. The latter seems to be more probable as the D series composites contain much less air [8]; nevertheless their dielectric constant is lower. It may be that natural polycrystalline CaCO₃ has a somewhat lower permittivity than monocrystalline calcite.

In the case of the dried samples, one would expect that an interfacial loss mechanism would be due to the conductivity difference of PE and CaCO₃. This would lead to a Debye-like loss peak with a relaxation frequency of about 16 Hz and a loss maximum of about 1.4, if it is assumed that $v_2 = 0.3$ and $\sigma_2 = 10^{-10}$ ohm⁻¹cm⁻¹. However, the experimental data show markedly different behavior: losses are lower, no peak appears, and the shape of the loss curve is not Debye-like. This discrepancy can only be resolved if the conductivity of the filler particles is even lower than 10^{-10} ohm⁻¹cm⁻¹, an estimated value inferred from experimental data on calcite single crystals [7]. Low residual losses are most probably caused by strongly bound water since the magnitude of these losses are higher in those samples which are most sensitive to water adsorption under ambient conditions.

The interpretation of the dielectric data obtained using wet samples is even more complicated. In wet,

heterogeneous systems several different mechanisms can overlap [9]. Free water has its own relaxation process in the GHz region, which is very far from the frequencies used in our study. Relaxation times are much longer in ice or in adsorbed water [9, 10], but the dielectric losses still show maxima, depending on the temperature. Increasing temperatures shift the maximum frequencies toward higher values. In the present study no loss peak appeared as a function of frequency. Maxima can be observed in temperature dependent studies, but even there the peak height (but not its position) depends on measuring frequency (see also References [1]), so they are not true loss peaks, but are the result of two opposing effects: increasing mobility and decreasing water content. Similar behavior is observed in other moist heterogeneous systems [11] and the present interpretation is consistent with this. The possibility cannot be ruled out that the dipolar dielectric relaxation of adsorbed water molecules contributes to the observed loss, but one can be sure that this is not the dominating mechanism.

Taking the heterogeneous nature of the system into account, interfacial relaxation processes [6, 9, 10] must play an important role. Adsorbed moisture increases the surface conductivity of the filler particle, so that one would expect a higher relaxation frequency for these samples than for the dry samples. If the adsorbed layer is more than monomolecular, it can be regarded as a classical phase, and a three-phase interfacial relaxation model can be developed using a consecutive application of the complex analog of Equation (2). We have used this method in a previous study [1] but the result was discouraging. The assumption of a distinct water phase is quite reasonable; for a composite containing 60 wt % filler with an average particle diameter of 2.5 μm [1] the thickness of the water layer is about 30Å and 400Å for water contents of 0.1 and 1 wt % respectively. In comparing these values with atomic dimensions (1Å) the layers can be regarded as "phases". Another question to be answered is whether the water adsorption is confined to the surface layer or penetrates central parts of the sample. Diffusion of water in polyethylene is very low (2.3×10^{-11} m^2/s) [12] so one might expect that water cannot penetrate the sample on the time scale of a few days. Using the dielectric data presented in Figure 8 and the one-dimensional diffusion model [12], the estimated diffusion coefficient of the D62 composite is of the order of 10^{-12} m^2/s which is even lower than that of PE, quoted above. The diffusion coefficients of composites containing impermeable fillers are usually lower than those of the pure

matrix [12]. Even with a low diffusion coefficient, a relatively thick (0.75 mm) sample took up more than 90% of the equilibrium water content in two days so one can be sure that water adsorption is not confined to those filler particles close to the surface of the composite.

The presence of water can complicate the interfacial mechanism not only by forming a distinct phase at the boundaries but also by dissolving ions from the filler. The migration of these ions under the effect of an external force can lead to very high dispersion and loss [11, 13]; the relaxation time is influenced by the diffusion coefficient of the dissolved ions in the electrolyte solution. This type of polarization can be characterized by a continuous relaxation time spectrum [13, 14], i. e. a non-Debye curve. The mean relaxation time can be estimated by the following formula [13]:

$$\tau_D = \frac{\underline{a}^2}{2\bar{D}} \tag{3}$$

where $\underline{a}$ is the radius of the particles and $\bar{D}$ is the average diffusion coefficient of the ions calculated as [13]:

$$D = \frac{D^+ D^- (z^+ + z^-)}{z^+ D^+ + z^- D^-} \tag{4}$$

where D^+, z^+ and D^-, z^- are the diffusion coefficients and charges of cations and anions, respectively. If for example, the dissolved ions are Ca^{2+} and CO$_3^-$ $z^+ = z^- = 2$, $D^+ = 7.9 \times 10^{-10}$ m^2/s, $D^- = 9.2 \times 10^{-10}$ m^2/s [15] and using $\underline{a} = 1.25$ μm [1] the τ_D resulting from Equation (3) is 9.2×10^{-4} s, indicating that the loss maximum can be expected at around 170 Hz. This theory was originally developed for dilute aqueous suspensions, but a simplified theory was also proposed for particles covered by thin adsorbed films containing dissolved ions [13]. In the simplified theory the time constant of the loss process is given by:

$$\tau = \frac{\tau_D}{1 + \varkappa^2 \, \underline{a} \, h\varepsilon_w/(2\varepsilon_1 + \varepsilon_2)} \tag{5}$$

where τ_D is the time constant for diffusion described in Equation (3), $\varkappa$ is the inverse Debye radius [15], h is the thickness of the adsorbed water layer, ε_w is the permittivity of water and ε_1, ε_2 and $\underline{a}$ have their usual meaning. Again assuming a saturated CaCO$_3$ solution and $h = 30$ Å, the relaxation time is 4.4×10^{-6} s, thus the peak should appear at 36 kHz. This value is remarkably close to the relaxation time obtained using a

simple three phase model for a system containing 0.1 wt % water, 60 wt % filler, if the conductivity of the water layer corresponds to that of the saturated $CaCO_3$ solution [1]. All of these predicted frequencies are too high; no loss peak has been observed in the 100 kHz – 20 Hz frequency range. Interestingly, soaking the samples in NaCl solution did not change the dielectric properties significantly (see Fig. 11); it appears that the conductivity of the soaking medium has only a secondary effect.

In addition to the incorrect prediction of relaxation times, another problem with the interfacial models is that they all result in a constant permittivity at low frequencies, which is again in contradiction to the experimental results. Assuming either conductive filler particles or nonconductive particles with thin conducting surface layers in a non-conductive medium, the low frequency limiting permittivity can be calculated from the complex analog of Equations (1) or (2) [6]. In the case of Equation (1) the low frequency limiting permittivity for the highly conductive filler/nonconductive matrix condition is given by [16]:

$$\bar{\varepsilon}_s = \frac{\varepsilon_1}{(1 - v_2)^3} \tag{6}$$

Assuming 60 wt % filler with a density of 2.71 g/cm³ and using $\varepsilon_1 = 2.2$ and a density of 0.94 g/cm³ for the matrix [4] $\bar{\varepsilon}_s$ is 7.7. The observed low frequency permittivities were higher than this value for the D62 samples, but were much lower for the other samples.

One must look for the reason for these discrepancies, since the complex Bruggeman or Hanai Equation (16) proved to be successful in describing the dielectric behaviour of concentrated emulsions, including three phase systems consisting of encapsulated particles [17]. The non-Debye shape of the dielectric loss curves in the present study can arise from the electrical interactions between the filler particles. The original Maxwell-Wagner model assumed that the systems were dilute and that there were no interactions between the particles [6]. The electrical interactions can be treated in the same way as ordered arrays of monodisperse particles but the mathematical difficulties are large [18]. These interactions are taken into account indirectly in the Hanai theory [16] where there is no explicit expression for the relaxation time. In fact, according to calculations using the Hanai equation there are deviations from the Debye-shape at high concentration of the filler [19].

In those theories which take into account surface conductivities or counter ion polarization effects [11,13] the relaxation time depends on the size of the particles so that a distribution in the particle size results in a distribution in relaxation times. As shown by electron microscope studies [20] a particle size distribution does exist in these composites; in the case of the D samples the average diameter is 2.3 μm and the maximum diameter is 15 μm, while in the case of the H series these figures are 2.5 μm and 45 μm, respectively.

Other factors which cannot be explained by integral methods, are the clustering of the particles and the formation of continuous networks. The first effect can be calculated, at least in principle, by the Nielsen method [21]; the second effect is the central problem of percolation theory [22,23]. According to Nielsen [21] agglomeration increases the viscosity of suspensions [24], and analogously increases the static dielectric constant. This theory is based on an analogy between mechanical and electrical processes and on the assumption that the depolarization ratio [6] of agglomerated particles is analogous to the reciprocal Einstein coefficient [24] of the same aggregates. However, even this correction would only increase somewhat the limiting permittivity; it would not yield a continously increasing permittivity at low frequencies.

The percolation theory concentrates, not on agglomeration in general, but on the appearance of continuous conducting paths in heterogeneous mixtures of materials having very different conductivities. Using the effective medium theory the following formula has been derived for mixtures of oriented spheroids [23]:

$$(1 - A)\,\bar{\varepsilon}^2 + [\varepsilon_1(A - v_1) + \varepsilon_2(A - v_2)]\bar{\varepsilon}$$
$$+ \varepsilon_1\varepsilon_2 A = 0 \tag{7}$$

where ε_1 and ε_2 have their usual meaning, v_1 and v_2 are the volume fractions of the components and A is the depolarization factor [6] which is 1/3 for spheres. As one can see, the effective medium theory is symmetrical in the indices and there is no sharp distinction between matrix and filler, as in the case of Equation (1). By assuming a conductive filler $(\sigma_2 \gg \sigma_1)$ in a dielectric medium, taking the complex analogue of Equation (7) and separating the real and imaginary parts the following equations can be derived for the conductivity and permittivity of the composite [23]:

$$\bar{\sigma} = 0 \qquad\qquad \text{if } 0 \leq v_2 \leq A$$
$$\bar{\sigma} = \frac{\sigma_2(v_2 - A)}{1 - A} \qquad \text{if } A \leq v_2 \leq 1 \tag{8}$$

$$\bar{\varepsilon} = \frac{\varepsilon_1 A}{A - v_2} \qquad \text{if } 0 \le v_2 \le A$$

$$\bar{\varepsilon} = \frac{\varepsilon_1 v_2 (1 - v_2)}{(1 - A)(v_2 - A)} \qquad \text{if } A \le v_2 \le 1 \qquad (9)$$

There is an insulator-conductor transition or percolation threshold at $v_2 = A$ in the case of spheres with $v_2 = 0.33$. This corresponds to about 60 wt% filler for these studies. It is at least possible that in the D62 sample the filler particles (and consequently the water phase on the surfaces of the particles) form a continuous phase between the electrodes. It is interesting to note that near the percolation threshold $\bar{\varepsilon}$ diverges as $|v_2 - A|$, which can, perhaps, account for the large permittivity of D62.

If the particles of an aggregate are not in direct (metallic) contact, but interact strongly through space, the aggregate can be treated as an ellipsoid [25]; the depolarization factors [6] depend on the mode of packing (e. g. linear fc c cubic etc.). If the particles of the aggregate are in contact with each other, the system can be treated as a matrix inclusion type composite with a shape factor distribution [26, 27], but to do this one has to know the distribution fuction. It has been pointed out that the hypothesis of clustering (which can be observed in electron micrographs [20]) can help in explaining the observed phenomena; low frequency anomalies may be due to intra-cluster space charge phenomena.

Another possible interpretation of the phenomena observed in our study is in terms of the universal response theory [28]. By analyzing experimental data, it was concluded that Debye-like responses are virtually absent in condensed systems. It was stated that the dielectric properties can usually be described satisfactorily by the following formula:

$$\varepsilon^*(\omega) = \varepsilon_\infty + B(i\omega)^{n-1} \qquad (10)$$

with $0 < n < 1$. This type of response can be characterized by linear Cole-Cole plots, similar to those plotted from experimental data. A higher value of n corresponds to a lower slope [28]. In this form the equation is just a phenomenological representation of the experimental data, unless the underlying theoretical background is found. The first theoretical explanation was the semiqualitative "screened hopping model" [29], and the most recent explanation is the "cluster model of dielectric relaxation" [30] based on very general quantum and statistical theoretical arguments.

Jonscher [28] divided materials roughly into two classes: normal dielectric solids and carrier dominated systems. In the first class at lower frequencies ε' becomes constant and ε'' decreases according to a fractional power law. In carrier dominated systems, however, the dispersion remains continuous and n can even decrease. This low frequency process cannot be equated with simple ohmic conduction; even if n is close to zero; as in the case of classical ohmic conduction ε' remains constant. This type of behavior has been observed in various disordered systems containing partially mobile charge carriers such as amorphous semiconductors, inorganic and organic glasses, fast ionic conductors and wet heterogeneous systems [28]. High frequency losses are attributed to more localized, hopping-like motions while the low-frequency, strongly dispersive process is a near DC transport. These two processes run essentially parallel, transport dominates at low frequencies. If, however, barrier effects play an important role, a plateau can appear at intermediate frequencies, both in ε' and ε'' [28].

The cluster model [30] has been applied to explain the observed dielectric behavior in low dimensional disordered solids [31], for example heterogeneous systems containing adsorbed water [32]. This model assumes that water adsorbs in clusters, the high frequency process with higher n is due to the intracluster motion of protons, while at low frequencies the correlation length of proton motion exceeds the size of clusters; the inter-cluster motion becomes the dominating mechanism. Near DC conduction in this case assumes the existence of a continuous path between the two electrodes.

It has been found experimentally [28, 32] that dielectric losses measured at different relative humidities can be superposed on a single master curve by horizontal shifting, which helps to establish the form of the loss process in a wider frequency range. Superposition is also possible for our experimental data, as shown by the Cole-Cole plots compiled from the measurements on samples containing different amounts of water. Figure 16 shows the dielectric loss master curve for D62 and D20(62) samples. It is interesting to note that D20(62) prepared from D62 by mixing with Hifax-1900 can be normalized to the same curve as D62. Another important fact is that the n exponent in Equation (10) increases, rather than decreases with decreasing frequency in contrast to wet, porous or granular systems [28, 32]. This may be an indication of barrier or interfacial effects; the filler particles and the adsorbed water phase may not form a continuous path (which is

evidently impossible for D20(62) but quite possible for D62) so that an electrical transport process through the sample is impossible.

Conclusion

The comparison of experimental results with the existing theories has shown that none of the theories can account for all of the observed phenomena.

Simple interfacial theories cannot explain the large difference between the *D* and *H* samples, or between D62 and D48 samples and the non-Debye behavior. Modifications of this theory which take into account the effect of dissolved ions in the adsorbed layer, do not yield acceptable time constants. The discrepancy could be due to different mobilities of ions in solution and in the adsorbed layers; but since no detailed information is available about the electrochemical conditions at the filler surface, improvement of the theoretical description is not yet possible.

The universal response theory and the cluster-adsorption theory offer an interesting alternative. The problem with these models is just their "universality"; they do not take into account the heterogeneities of the system, so that one cannot interpret the results in terms of structural characteristics.

These results indicate that the adsorbed water certainly gives rise to the observed dispersion and loss, but quantitative interpretation of the data is still equivocal. DC dielectric and thermally stimulated current studies, to widen the frequency range and to study the effect of evaporated electrodes, are in progress and will be published elsewhere [33].

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