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Characterization of dielectric materials

ROBERT M. HILL
Chealsea College, Department of Physics, Pulton Place, London SW6 5PR, UK

Recent examination of the form of the dielectric susceptibility as a function of frequency has shown the presence of power law behaviour at both low and high frequencies, with respect to the frequency of maximum loss. The magnitudes for the power law exponents of one hundred dielectric loss peaks are reported together with relevant experimental information. It is observed that very few materials show the characteristics of the standard susceptibility functions.

1. Introduction

Recent analysis of experimental measurements of dielectric properties in a wide range of materials, under various experimental conditions, has shown that the imaginary part of the dielectric susceptibility $\chi''(\omega)$, can be represented in the form of power laws of the measuring frequency, ω, except in a region around the loss peak frequency ω_p [1–3]. The power law behaviour has been expressed as

$$\chi''(\omega) \propto \omega^m ; \omega \ll \omega_p \qquad (1)$$

and

$$\chi''(\omega) \propto \omega^{-(1-n)}; \omega \gg \omega_p. \qquad (2)$$

The exponents m and n are characteristic parameters for the particular material under investigation under the specific conditions of examination and, together with ω_p and the zero frequency magnitude of the susceptibility, $\chi'(0)$, give a complete characterization of the susceptibility process [4, 5]. It has been proposed [4] that the characteristic parameters m and n are, respectively, the co-ordination fractions of multiple flip–flops and single flips of the dipolar species under examination in the material. The term "flip" defines a single re-orientation process whereas "flip–flop" is defined, by analogy with a spin exchange process, as an alteration in the structure surrounding a pair of dipoles such that the local fields at the two sites deviate from their average value although the nett orientation of the pair of dipoles remains unchanged.

As the characteristic parameters are both normalized they are constrained to lie in the range from zero to unity, with zero representing a complete lack of correlation and unity representing total correlation of the particular process. In the region of the peak loss these power law relationships no longer hold. This transition region is characterized by a maximum in $\chi''(\omega)$. The power law relationships given in Equations 1 and 2 are approximations based on the asymptotic behaviour at low and high frequencies. The complete complex susceptibility as a function of frequency has been determined [4, 5] and will be examined in detail elsewhere.

2. The survey

More than one hundred published sets of susceptibility data have been examined and their characteristic exponents determined. One hundred of these sets of values, together with relevant experimental information where this is considered to be of significance, are reported here. Table I lists this information and Fig. 1 presents a plot of the exponents m and $(1-n)$ for this data. In Fig. 1 the size of the data points gives an indication of the accuracy of exponent evaluation. If the correlation parameters were totally unrelated Fig. 1 would exhibit a perfectly random distribution of uniform density. It is apparent on inspection of the diagram that this is not the case. For a particular data pair the magnitude of m is, generally, greater, than the magnitude of $(1-n)$, although there are a few cases in which the converse applies. The generality of the observations is shown by the clustering of the datum points into the upper left

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TABLE 1 The characteristic exponents m and $(1-n)$ for the materials shown in Fig. 1 together with the references and experimental data

Number in Fig. 1	Material	m	$(1-n)$	Comments	Reference number
1	Polyacetaldehyde	0.64	0.54	Amorphous form	7
2	Polyacronitrile	0.18	0.33		8
3	Polyethylene	0.82	0.35	$1.3 < T < 17.1$ K Sample PE1	9
4	Polyethylene	0.66	0.53	$29 < T < 4200$ mK Sample PE 10Ma	9
5	Polyethylene	0.68	0.63	$20 < T < 4200$ mK Sample PE 14	9
6	Polyethylene terephthalate	0.77	0.28	α-peak	10
7	Polyethylene terephthalate	0.42	0.08	β-peak	10
8	Methyl methacrylate	0.25	0.33		11
9	Polymethyl acrylate	0.74	0.25		12
10	Polymethyl methacrylate	0.66	0.28	$100 < P < 2950$ atm, $283 < T < 363$ K	13
11	Polymethyl methacrylate	0.45	0.17		14
12	Poly-*n*-butyl methacrylate	0.71	0.29		15
13	Polychloroprene	0.38	0.23	α-peak	16
14	Polychloroprene	0.17	0.16	β-peak	16
15	Polydian carbonate	0.62	0.21	α-peak	17
16	Polyethyl methacrylate	0.49	0.18		18
17	Poly-*n*-nexyl methacrylate	0.90	0.35		19
18	Poly-*n*-octyl methacrylate	0.84	0.38		19
19	Poly-cyclohexyl methacrylate	0.068	0.25		20
20	Poly-2-chlorocyclohexyl methacrylate	0.32	0.44		20
21	Poly-4-chlorocyclohexyl methacrylate	0.23	0.31		20
22	Poly-4-chlorocyclohexyl acrylate	0.42	0.25		20
23	Polypropylene	0.37	0.24		21
24	Polypropylene carbonate	0.90	0.45	α-peak	22
25	Polypropylene carbonate	0.85	0.71	β-peak	22
26	Polypropylene oxide	0.39	0.31		23
27	Polyvinyl acetate	0.83	0.43		12
28	Polyvinyl acetate	0.76	0.38	In solution in Galva 15	24
29	Polyvinyl acetate	0.56	0.42	In solution in Galva 60	24
30	Polyvinyl acetate	0.50	0.29		25
31	Polyvinyl flouride	0.28	0.11		26
32	Polyvinylidene flouride	0.07	0.49	α-peak	27
33	Polyvinylidene flouride	0.53	0.13	β-peak	27
34	Polyvinylidene flouride	0.05	0.12	γ-peak	27
35	Polyvinyl formal	0.25	0.24		25
36	Polyvinyl chloroacetate	0.57	0.40		12
37	Polyvinyl chloroacetate	0.60	0.43		24
38	Polyvinyl chlorodiphenyl	0.24	0.22		28

TABLE I (continued)

Number in Fig. 1	Material	m	$(1-n)$	Comments	Reference number
39	Poly-γ-benzyl-L-glutamate	0.42	0.81	Solid form	29
40	Poly-γ-benzyl-L-glutamate	0.55	0.51	In solution in E.D.C.	30
41	Poly-γ-benzyl-L-glutamate	0.79	0.55	In solution in dioxane	30
42	Butyl stearate	0.56	0.77	$\omega_{\mathrm{p}} < 10^9$ Hz	31
43	Butyl stearate	1.0	0.33	$\omega_{\mathrm{p}} > 10^9$ Hz	31
44	Cyclohexyl chloride in polystyrene	0.47	0.30	α-peak	32
45	Cyclohexyl chloride in polystyrene	0.21	0.08	β-peak	32
46	Phthalic anhydride	0.87	0.45	3.72 wt%	33
47	Nylon 610	0.60	0.57	$T = 483$ K ($T_{\mathrm{m}} = 497.8$ K)	34
48	Nylon 610	0.30	0.51	$T = 413$ K	34
49	Nylon 610	0.18	0.41	$T = 373$ K	34
50	P-methoxyphenylazoxy-p-butylbenzene	0.75	0.77	Nematic phase	35
51	P-methoxyphenylazoxy-p-butylbenzene	0.60	0.81	Isotropic phase	35
52	*N*-heptyl-cyanobiphenyl	0.97	0.68	Both isotropic and nematic phases	36
53	Acetic acid	1.0	0.35	$\omega_{\mathrm{p}} > 10^9$ Hz	37
54	Bromobenzene in decalin	0.71	0.28		38
55	Chlorobenzene-pyridene	0.93	0.35	α-peak 43.4 conc.	39
56	Chlorobenzene-pyridene	0.15	0.10	β-peak 43.4 conc.	39
57	Chlorobenzene-cis-decalin	0.89	0.19	α-peak	40
59	Chlorobenzene-cis-decalin	0.06	0.15	β-peak	40
59	2-Methyl-3-heptanol	0.78	0.27	$P = 2.5$ kb	41
60	2-Methyl-3-heptanol	1.0	0.38	$P = 4.4$ kb	41
61	3-Methyl-3-heptanol	0.86	0.33	α-peak	40
62	3-Methyl-3-heptand	0.49	0.34	β-peak	40
63	5-Methyl-3-heptanol	0.90	0.67	α-peak	40
64	5-Methyl-3-heptanol	0.23	0.25	β-peak	40
65	5-Methyl-3-heptanol	0.65	0.68	$P = 3.55$ kb	41
66	5-Methyl-3-heptanol	0.98	0.57	$P = 1.57$ kb	41
67	Tricyclohexyl carbinol	1.0	0.83	$10^9 < \omega < 10^{11}$ Hz; $T > 176$ K	42
68	Tricyclohexyl carbinol	1.0	0.74	$\omega < 10^6$ Hz; $T < 108$ K	43
69	Neo-hexanol	0.72	0.95	β-peak	43
70	Glycerol	0.55	0.46	$P = 3.1$ kb	44
71	Glycerol	0.50	0.69	$P = 4.4$ kb	44
72	Menthol	0.99	0.22		45
73	2:4:6-tri-t-butylphenol	1.0	0.66	$10^9 < \omega < 10^{10}$ Hz; $176 < T < 293$ K	42
74	*n*-docosyl bromide	0.47	0.63		46
75	Picric acid	0.85	0.79		47
76	Polyethylene adipate	0.06	0.09		48

TABLE I (continued)

Number in Fig. 1	Material	m	$(1-n)$	Comments	Reference number
77	M.B.B.A.	0.85	0.73		49
78	Methyl stearate	0.57	0.47	$P < 2$ kb; $213 < T < 243$ K	50
79	Polyvinyl acetyl	0.45	0.24	$343 < T < 393$ K	25
80	Pnacol hydrate	0.89	0.86		51
81	Pentachlorotouene	0.87	0.64		52
82	Trichloroethane–cyclohexane	0.59	0.53	Cocn. range 1:1 to 0.8:1	53
83	Trichloroethane–cyclohexane	0.83	0.74	Cocn. range 0.4:1 to 0.2:1	53
84	Suprasil glass	0.15	0.31	$20 < T < 4200$ mK	9
85	Impurity cations in quartz	0.69	0.85		54
86	Silicon monoxide/platinum cermet film	0.54	0.71		55
87	Silicon p–n junction	0.83	0.78		56
88	Silicon p–n junction	0.16	0.60		56
89	Anodised tantalum	0.42	0.36		57
90	Anodised aluminium	0.58	0.92		57
91	Rochelle salt	1.0	0.96		58
92	KD_2PO_4	1.0	0.93		59
93	Triglycene sulphate	0.97	0.99		60
94	M.A.S.D.	0.81	0.75	$138 < T < 200$ K	62
95	$AgNa(NO_2)_2$	0.90	0.68		62
96	$AgNaNO_2$	1.0	0.83		63
97	$BaTi_7MgO_{16}$	0.68	0.55		64
98	H_2O	0.96(3)	0.96(8)	293 K selected published values	65
99	H_2O	0.78	0.76	181 K	66
100	D_2O	0.94	0.95	$T < 262.3$ K	67

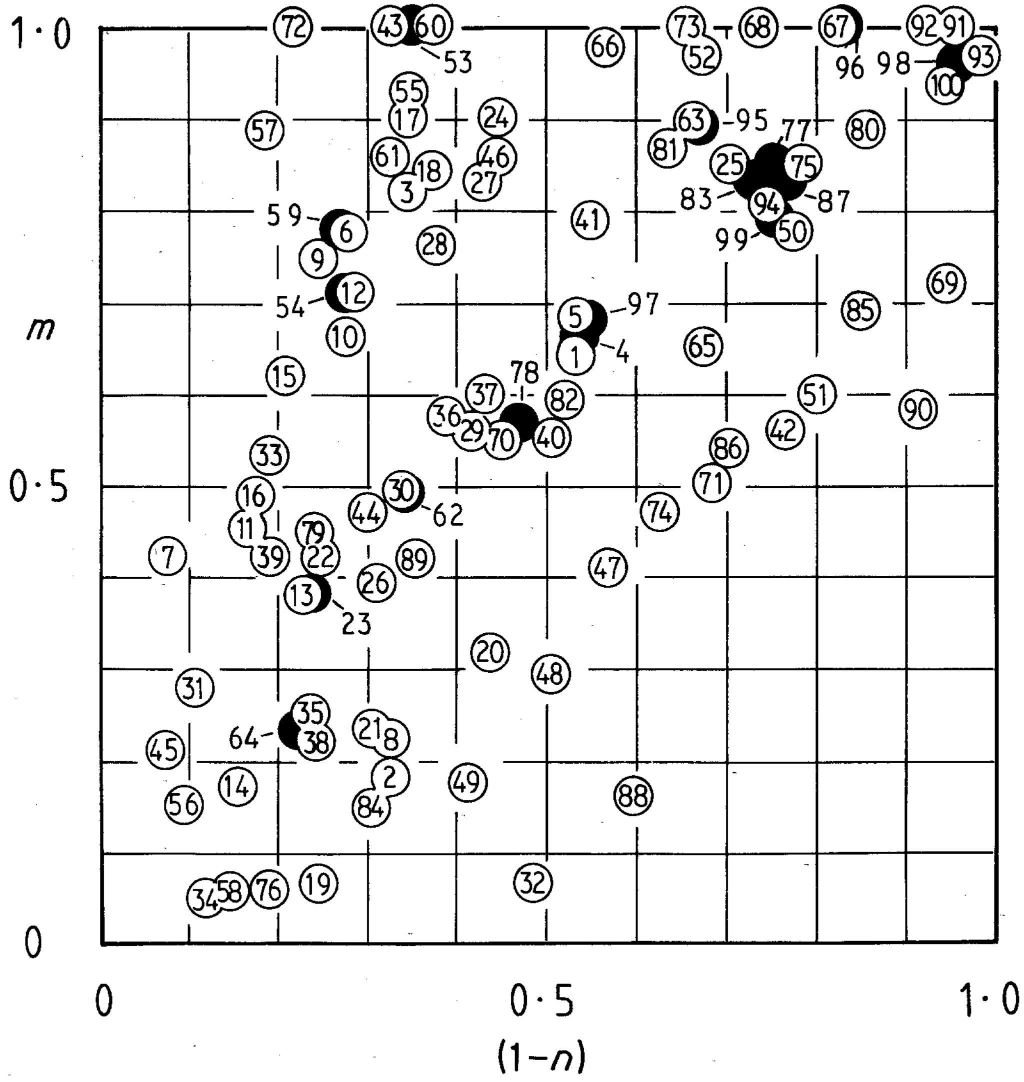

Figure 1 Presentation of the characteristic exponents m and $(1-n)$ for one hundred dielectric loss processes. The key to the data points is given in Table I and the size of the circles indicates the accuracy of evaluation of the exponents. Where it has not been possible to label the circles internally they have been filled in and the label written at the side. The Debye process occurs at the point given by $m = (1-n) = 1.0$; the Davidson–Cole characteristic is the line $m = 1.0$; the Cole–Cole characteristic is the line $m = (1-n)$.

hand region of the plot. It should be noted, however, that the upper left hand side is completely free of datum points.

The particular data presented here has been chosen to be representative of the published information available. In all cases the susceptibility curves were normalized [3] with respect to an external variable, typically temperature, to increase the accuracy of exponent evaluation. A number of sets of data have been chosen where information was presented for more than a single loss process. For example, the pair of datum points (13) and (14) are the characteristics for the α and β processes in polychloroprene. The α-peak, which is generally considered to be sharper than the β-peak, has larger values of m and $(1-n)$ than the β-peak. There appears to be no obvious relationship between the magntides of the characteristic parameters. Data has also been presented for a material in different solvents, the data points (28) and (29) and (40) and (41) being chosen on this basis. In both cases it can be seen that the parameter m changes more than the parameter $(1-n)$ under the solvent change. The effect of temperature, in the region of the melting point of a polymer, is indicated by (47), (48) and (49) which show that as the temperature is raised, the exponents both increase and fit the Debye model more closely. The case that behaves exactly as the Debye model, with $m = (1 - n) = 1.0$, has not been observed in this examination of the susceptibility of solids and liquids.

The many-body, correlated theory of dielectric response [4] has predicted that when the loss peak frequency is sufficiently high, of the order of 10^9 Hz or greater, the flip–flop process will not have sufficient time to develop and the parameter m will degenerate to a value of unity. Of the ten data points lying on the line $m = 1.0$ in Fig. 1, only the two sets of data (60) and (68) were not observed in the high frequency range. The flip–flop processes in 2 methyl–3 heptanol and in tricyclohexyl carbinol are perfectly correlated. The general case of $m = 1.0$ is referred to as the Davidson–Cole characteristic.

The materials listed in Table I have been arranged in broad groups. The major part of the published work on dielectric properties has been carried out on polymeric materials which are presented in the first paper part of Table I. Most of this information has $(1 - n)$ values of less than 0.5. Ferroelectric materials, on the other hand, tend to have large values of both m and $(1 - n)$ and are presented in the data group (88–97). The H_2O and D_2O results, (98–100), also have large values of the exponents and exhibit the further property that $m \approx 1 - n$, which is the characteristic of the Cole–Cole [6] susceptibility function. The Cole–Cole condition can be re-expressed as $m + n = 1.0$ which, in terms of the co-operative model, requires that any dipolar transition that is not of the flip–flop form must be a flip process. In this particular case the two re-orientation processes are mutually exclusive but include all possible re-orientations.

3. Concluding remarks

Extensive work has been presented in the literature on the analysis of dielectric relaxation by thorough consideration of the effects of experimental conditions such as temperature and pressure on the maximum loss frequency and of the magnitude of the susceptibility. It has been known, for some considerable time, that the shape of the susceptibility as a function of frequency plots were not of the Debye-form for most solids and liquids. Characterization of the shape, in terms of the parameters m and $(1 - n)$, as presented here, allows this information to be presented quantitatively and to be examined in terms of the experimental conditions. This can only strengthen our knowledge of the fundamental processes of electrical charge adjustment and interaction within solids and liquids and hence our understanding of these materials.

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