

Simulation of Heterophase Polarization in Polymers

G. Bánhegyi and P. Hedvig

Research Institute of Plastics, H-1950, Budapest, Hungary

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SUMMARY

A computer simulation program for calculating the temperature and frequency dependent dielectric properties of two-component composites containing spherical inclusions is described. Both components may exhibit ohmic conduction and Debye-like dispersion besides the interfacial polarization. Assumptions used in the simulation are discussed and some peculiar features of the resulting spectra are demonstrated by numerical examples.

INTRODUCTION

Mechanical properties of two-phase composites have been extensively studied during the last years. Relatively less attention is paid to their electrical properties, although these are highly dependent on the homogeneity of the sample. At the interface of two substances having different conductivities and permittivities under the influence of an external field dipoles are formed. This phenomenon is the so-called interfacial- or Maxwell-Wagner /MW/ polarization. The importance of taking into account the MW effect in interpreting dielectric spectra of heterogeneous polymeric systems /blends, block copolymers, filled, reinforced and plasticized polymers/ has been stressed among others by NORTH et al./1978/, HEDVIG /1980/, LILAONITKUL and COOPER /1979/ and PILLAI et al./1981/.

THEORETICAL

The dielectric properties of heterogeneous systems have been reviewed by VAN BEEK /1967/. The MW complex permittivity in several cases can be written as simple Debye equation. The

position and magnitude of the MW-peak strongly depend on the shape and concentration of the inclusions but not on their size. The complex dielectric permittivity of systems containing dispersed spheres randomly distributed in a medium has been given by WAGNER /1914/. The Wagner formula is limited to small concentration of the inclusions. An extension of this theory to the higher concentrations was achieved by HANAI /1968 and references therein/ using a complex integration scheme. The resulting expression is a complicated third-order complex equation which is difficult to handle:

$$\left[\frac{\bar{\epsilon}^* - \epsilon_2^*}{\epsilon_1^* - \epsilon_2^*} \right]^3 \frac{\epsilon_1^*}{\bar{\epsilon}^*} = /1 - v_2/^3 \quad /1/$$

where $\bar{\epsilon}^*$ denotes the permittivity of the system as a whole, ϵ_1^* refers to the matrix, ϵ_2^* to the inclusion, v_2 is the volume fraction of the dispersed particles.

As the main problem in the dielectric spectroscopy of heterogeneous polymeric media is to distinguish between the loss peaks of the components and the interfacial one a computer simulation system was developed to estimate the effect of different parameters on the resulting properties. Instead of solving the Hanai equation exactly the simulation was made under the following assumptions:

a./ The complex permittivity of the system can be described by a Debye-type equation:

$$\bar{\epsilon}^* = \bar{\epsilon}_\infty + \frac{\bar{\epsilon}_s - \bar{\epsilon}_\infty}{1 + j\omega\bar{\tau}} + \frac{\bar{\sigma}_s}{j\omega\epsilon_0} \quad /2/$$

where ϵ_0 is the vacuum permittivity, $\bar{\epsilon}_\infty$ is the high-frequency limiting permittivity /HANAI, 1968/:

$$\left[\frac{\bar{\epsilon}_\infty - \epsilon_2'}{\epsilon_1' - \epsilon_2'} \right]^3 \frac{\epsilon_1'}{\bar{\epsilon}_\infty} = /1 - v_2/^3 \quad /3/$$

ϵ_1' and ϵ_2' denote the real parts of component permittivities/
 $\bar{\epsilon}_s$ is the low-frequency limiting permittivity /HANAI, 1968/:

$$\bar{\epsilon}_s \left[\frac{3}{\bar{\sigma}_s - \sigma_2} - \frac{1}{\bar{\sigma}_s} \right] = 3 \left[\frac{\epsilon_1' - \epsilon_2'}{\sigma_1 - \sigma_2} + \frac{\epsilon_2'}{\bar{\sigma}_s - \sigma_2} \right] - \frac{\epsilon_1'}{\sigma_1} \quad /4/$$

where $\bar{\sigma}_s$ is the low-frequency limiting conductivity of the system, σ_1 and σ_2 are the total conductivities of the components:

$$\left[\frac{\bar{\sigma}_s - \sigma_2}{\sigma_1 - \sigma_2} \right]^3 \frac{\sigma_1}{\bar{\sigma}_s} = 1 - v_2/3 \quad /5/$$

As there is no explicit expression for the MW relaxation time in the HANAI-approximation, $\bar{\tau}$ is estimated by the Wagner formula /VAN BEEK, 1967/:

$$\bar{\tau} = \epsilon_0 \frac{2 \epsilon_1' + \epsilon_2' - v_2 / \epsilon_2' - \epsilon_1'}{2 \sigma_1 + \sigma_2 - v_2 / \sigma_2 - \sigma_1} \quad /6/$$

b./ The dielectric dispersion ϵ_1' and conduction σ_1 of the components are themselves temperature and frequency dependent and are also approximated by Debye equations:

$$\epsilon_i^* = \epsilon_\infty^i + \frac{\epsilon_s^i - \epsilon_\infty^i}{1 + j\omega \tau_i} + \frac{\sigma_s^i}{j\omega \epsilon_0} \quad /7/$$

where ϵ_∞^i and ϵ_s^i are the high- and low frequency limiting permittivities of the components which are assumed temperature independent /the C/T type dependence of the oscillator strength is thus neglected/, σ_s^i is the ohmic conduction with an exponential temperature dependence /characterized by the σ_0^i preexponential factor and E_c^i activation energy/. The temperature dependence of the component relaxation times can be described by the Arrhenius or by the WLF equation /see e.g. HEDVIG, 1977/. The dispersion of the components is the most important in our calculations as earlier the MW-effect has been calculated with frequency independent conductivities and permittivities.

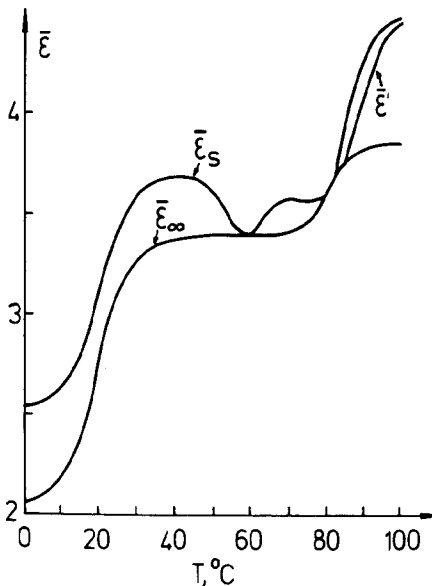
RESULTS AND DISCUSSION

Although simulation of frequency or temperature dependent spectra are equally possible we have focused our attention on the temperature dependent phenomena, as temperature dependent spectra are easily available on polymers. The characteristic functions gained from the simulation are the following:

a./ $\bar{\epsilon}_\infty/T/$ describes the permittivity of the mixture if the components are non-conductive.

b./ $\bar{\epsilon}_s/T/$ takes into account the ohmic conductivity and the dielectric loss of the components. Unlike $\bar{\epsilon}_\infty/T/$ $\bar{\epsilon}_s/T/$ is not necessarily a monotonous function of the temperature. Under the condition $\epsilon'_1/\epsilon'_2 = \sigma_1/\sigma_2$ which is fulfilled near to the component loss peaks the MW relaxation vanishes /see CLAUSSE,1975/.

c./ According to eq./2/ $\bar{\epsilon}'/T/$ describes the dispersion between $\bar{\epsilon}_\infty/T/$ and $\bar{\epsilon}_s/T/$. The peculiarity of this dispersion is that neither the oscillator strength, nor $\bar{\epsilon}$ is a monotonous function of the temperature. The actual shape of $\bar{\epsilon}_\infty/T/$, $\bar{\epsilon}_s/T/$ and $\bar{\epsilon}'/T/$ curves for a special system /system A of Table 1/ is shown on Fig.1. Overlap of the component- and MW trans-



itions is clearly visible.

d./ The MW $\bar{\epsilon}''/T/$ curve also differs from the usual dielectric absorption curves, as besides $(\epsilon_s - \epsilon_\infty)\omega\bar{\epsilon}/(1+\omega^2\bar{\epsilon}^2)$ $\bar{\sigma}_s/\epsilon_0\omega$ also exhibits maximum. This is a consequence of the dielectric losses of the components which are superimposed to their conductivities.

Fig.1. The limiting permittivities and dispersion curve for system A /Table 1/ at $v_2=0.3$ and $\nu=10$ Hz

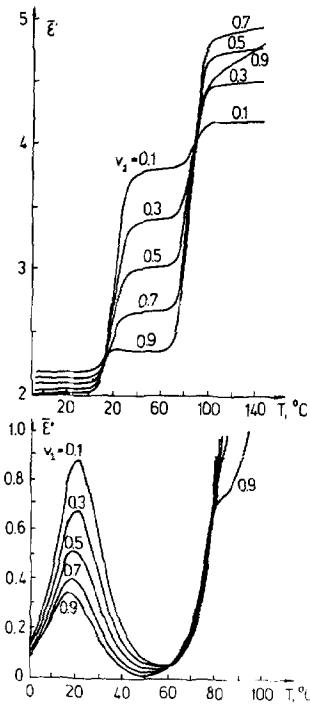


Fig.2 shows the dispersion and absorption curves of system A as a function of volume fraction of the inclusion. The only unexpected feature of the $v_2 = 0.9$ curve is the slow increasing tendency at higher temperatures

A phase inversion in system A results in dramatic changes of the dispersion and absorption curves /see Fig.3/. In this case the inclusions are more conductive which leads to high MW losses. The continuous increase in $\bar{\epsilon}'$ at high temperatures is

Fig.2./left/ Dispersion and absorption curves for system A as a function of temperature for $v_2 = 0.1 - 0.9$ and $\nu = 10$ Hz.

Fig.3./below/ Dispersion and absorption curves for the phase-inverted system A as a function of temperature at $v_2 = 0.5 - 0.9$ and $\nu = 10$ Hz

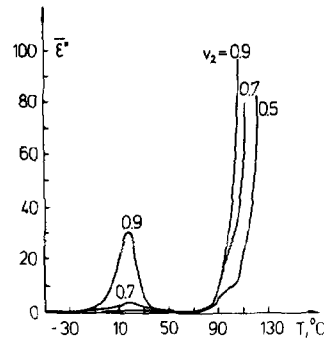
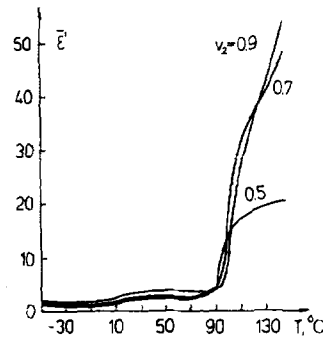


TABLE 1. Characteristic data of two composites

| property $i =$ | System A | | System B | |
|-------------------------------------|-----------------------|-----------------------|-------------------|----------------------|
| | 1 | 2 | 1 | 2 |
| ξ_s^i | 4.0 | 3.5 | 4 - 10 | 5 - 11 |
| ξ_∞^i | 2.0 | 2.2 | 3.0 | 2.0 |
| relax. type ⁺ | 83.7 | 167.5 | WLF | 251.2 |
| T_o^{++} /C°/ | 20 | 80 | 50 | 80 |
| σ^i / $\Omega^{-1}cm^{-1}$ / | 1.23×10^{17} | 2.43×10^{12} | 3.7×10^5 | 3.7×10^{10} |
| E_c^i /kJ/mol/ | 192.6 | 171.7 | 144.4 | 144.4 |

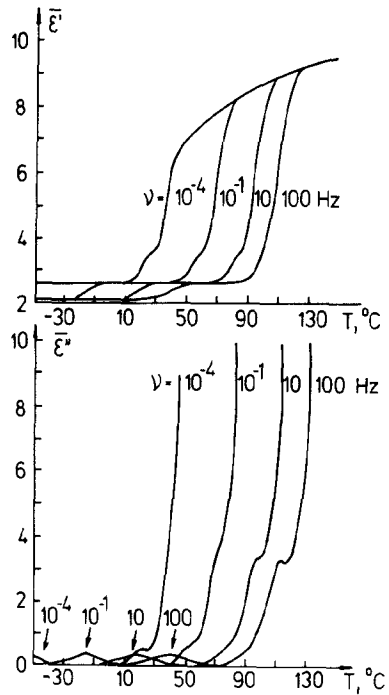
+ If Arrhenius type is assumed the activation energy of the relaxation is given in kJ/mol units. In the WLF case the universal constants are used

⁺⁺Transition temperature

really observed in filled rubbery systems.

The effect of measuring frequency on the spectra is shown on a phase-inversed system at $\nu_2 = 0.5$ /see Fig. 4/. By decreasing the frequency the resolution increases which draws attention to the low effective frequency isothermal or

Fig.4. The temperature dependence of dispersion and absorption curves for a phase-inversed system A at $\nu_2 = 0.5$ and $\nu = 10^2 - 10^{-4}$ Hz



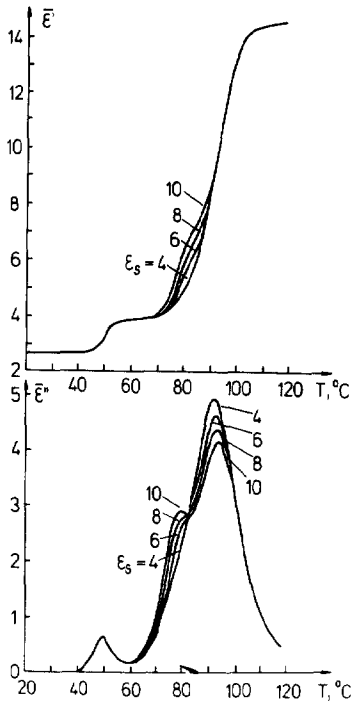
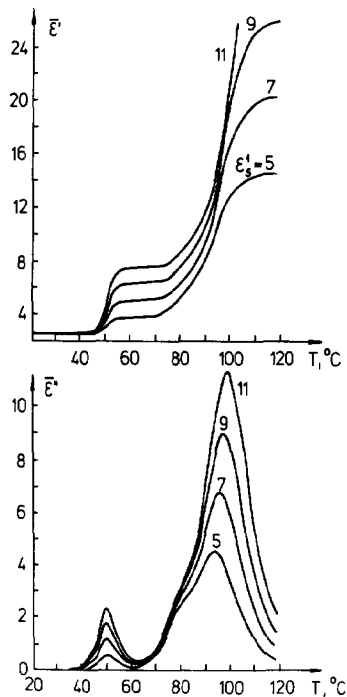


Fig.5./left/ The effect of polarity of the inclusion $\epsilon_s^2 = 4-10$ on the temperature dependent dispersion and absorption curves for system B /Table 1./ at $\nu_2 = 0.3$ and $\nu = 10$ Hz

Fig.6./below/ The effect of the polarity of the matrix $\epsilon_s^1 = 5-11$ on the temperature dependent dispersion and absorption curves of system B at $\nu_2 = 0.3$ and $\nu = 10$ Hz

thermally stimulated quasi-static methods /see e.g. HEDVIG and SOMOGYI, 1972/.

The effect of polarity of the phases on the spectra is shown on Figs.5 and 6 for another system /system B of Table 1./. In this case again the inclusions are more conductive than the matrix. One can clearly see from the figures that the effect of the polarity of the matrix is much more pronounced.



The present approximation may be helpful in forecasting the main tendencies, but for obtaining more realistic values an essential improvement in the assumptions is needed. A new simulation system of this type is under elaboration. Calculations starting from the experimental spectra of the pure components can solve practical problems too if sufficient information is gained on simple models.

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