The dielectric spectroscopy of epoxy composites with unoxidized graphene nanoplates

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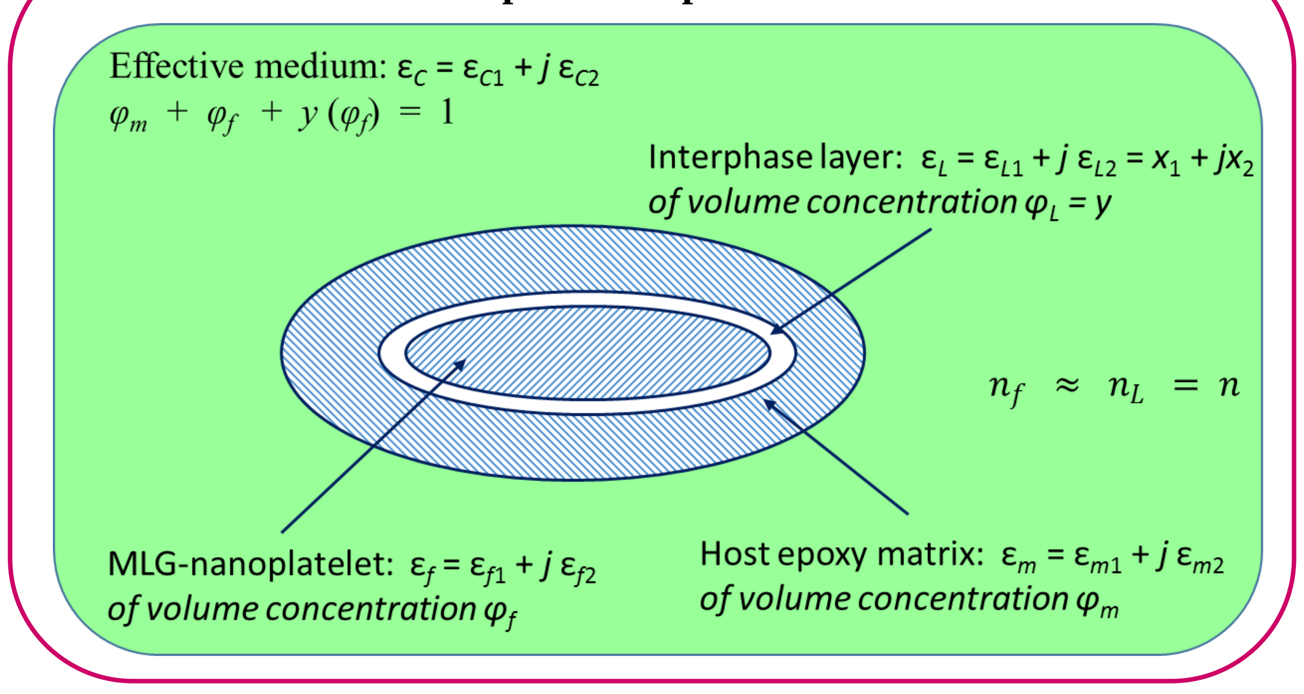
Abstract

The broad-band dielectric spectroscopy has been used as a tool to study molecular structure of epoxy nanocomposites filled with non-oxidized multilayered graphene nanoplates. Parameters of interphase area have been estimated by using the Steeman-Maurer model for a three-phase dielectric material

Three-phase composite material



The calculation scheme

The complex dielectric permittivity ε_C of a three-phase composite material is given by the Steeman-Maurer relation [1]

$$\varepsilon_C(n,\omega,\varphi_f,\varphi_L) = \frac{\varphi_f\cdot\varepsilon_f(\omega) + \varphi_L\cdot R(n,\omega)\cdot\varepsilon_L(\omega) + (1-\varphi_f-\varphi_L)\cdot S(\varphi_f,n,\omega)\cdot\varepsilon_m(\omega)}{\varphi_f + \varphi_L\cdot R(n,\omega) + (1-\varphi_f-\varphi_L)\cdot S(\varphi_f,n,\omega)}$$

$$R(n,\omega) = \frac{(1-n)\cdot\varepsilon_L(\omega) + n\cdot\varepsilon_f(\omega)}{\varepsilon_L(\omega)}$$

$$S(n,\omega,\varphi_f,\varphi_L) = \frac{[n\cdot\varepsilon_L(\omega) + (1-n)\cdot\varepsilon_m(\omega)]\cdot[n\cdot\varepsilon_f(\omega) + (1-n)\cdot\varepsilon_L(\omega)]}{\varepsilon_L(\omega)\cdot\varepsilon_m(\omega)} + \frac{n\cdot(1-n)\cdot\varphi_f\cdot[\varepsilon_L(\omega) - \varepsilon_m(\omega)]\cdot[\varepsilon_f(\omega) - \varepsilon_L(\omega)]}{(\varphi_f + \varphi_L)\cdot\varepsilon_L(\omega)\cdot\varepsilon_m(\omega)}$$

φ_f, φ_L – are volume concentrations for the filler and interphase area, respectively;
$\varepsilon_C, \varepsilon_m, \varepsilon_f, \varepsilon_L$ – are complex dielectric permittivity for the polymer—based composite material, the host polymer matrix, the filler, and the interphase area, respectively;
n is the depolarization factor [2] of the filler particle in the direction of an applied electric field of the circular frequency ω.

For the case of $n = 0$ we have $R(0,\omega) = S(0,\omega,\varphi_f,\varphi_L) = 1$ and

$$\varepsilon_C(0,\omega,\varphi_f,\varphi_L) = \varphi_f\cdot\varepsilon_f(\omega) + \varphi_L\cdot\varepsilon_L(\omega) + (1-\varphi_f-\varphi_L)\cdot\varepsilon_m(\omega)$$

For the case of $n = 1$ we have

$$R(1,\omega) = \varepsilon_f(\omega)/\varepsilon_L(\omega),$$

$$S(1,\omega,\varphi_f,\varphi_L) = \varepsilon_f(\omega)/\varepsilon_m(\omega)$$

$$\varepsilon_C(0,\omega,\varphi_f,\varphi_L) = \frac{1}{\frac{\varphi_f}{\varepsilon_f(\omega)} + \frac{\varphi_L}{\varepsilon_L(\omega)} + \frac{1-\varphi_f-\varphi_L}{\varepsilon_m(\omega)}}$$

Using the Steeman-Maurer relation and measured values of the dielectric permittivity $\varepsilon_{C1,m}(\omega,\varphi_f)$ and the dielectric loss factor $\varepsilon_{C2,m}(\omega,\varphi_f)$ of the composites, both the interphase layer's dielectric permittivity $\varepsilon_{L1}(n,\omega,\varphi_f,\varepsilon_{L2})$ and volume portion $\varphi_L(n,\omega,\varphi_f,\varepsilon_{L2})$ can be estimated by solving the set of equations

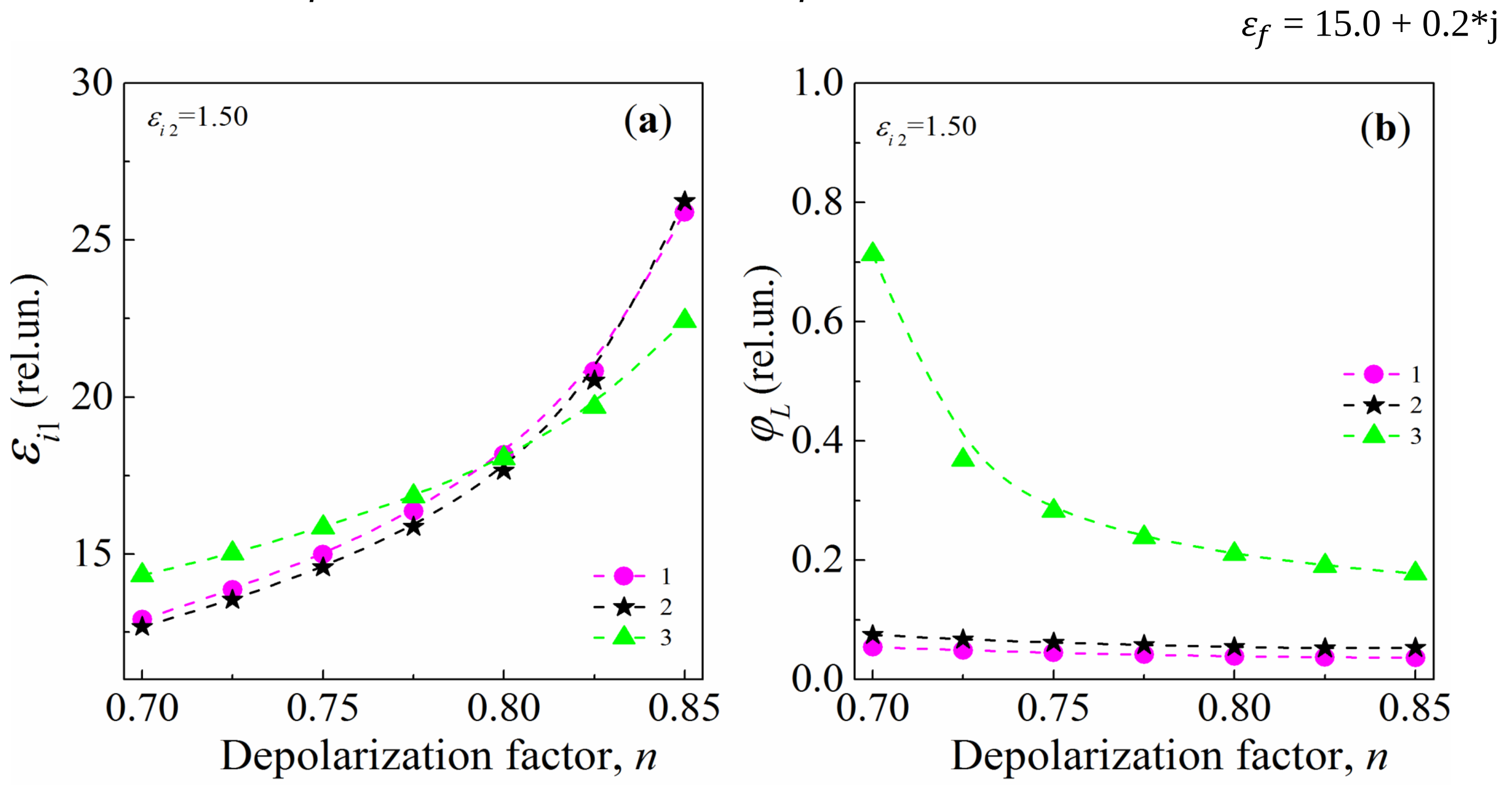
$$Re[\varepsilon_C(n,\omega,\varphi_f,\varphi_L,\varepsilon_{L2})] = \varepsilon_{C1,m}(\omega,\varphi_f)$$

$$Im[\varepsilon_C(n,\omega,\varphi_f,\varphi_L,\varepsilon_{L2})] = \varepsilon_{C2,m}(\omega,\varphi_f)$$

provided that n and ε_{L2} are prescribed as independent parameters.
Frequency-averaged dependences $\varepsilon_{L1}(n,\varphi_f,\varepsilon_{L2})$ and $\varphi_L(n,\varphi_f,\varepsilon_{L2})$ are plotted on the figures.

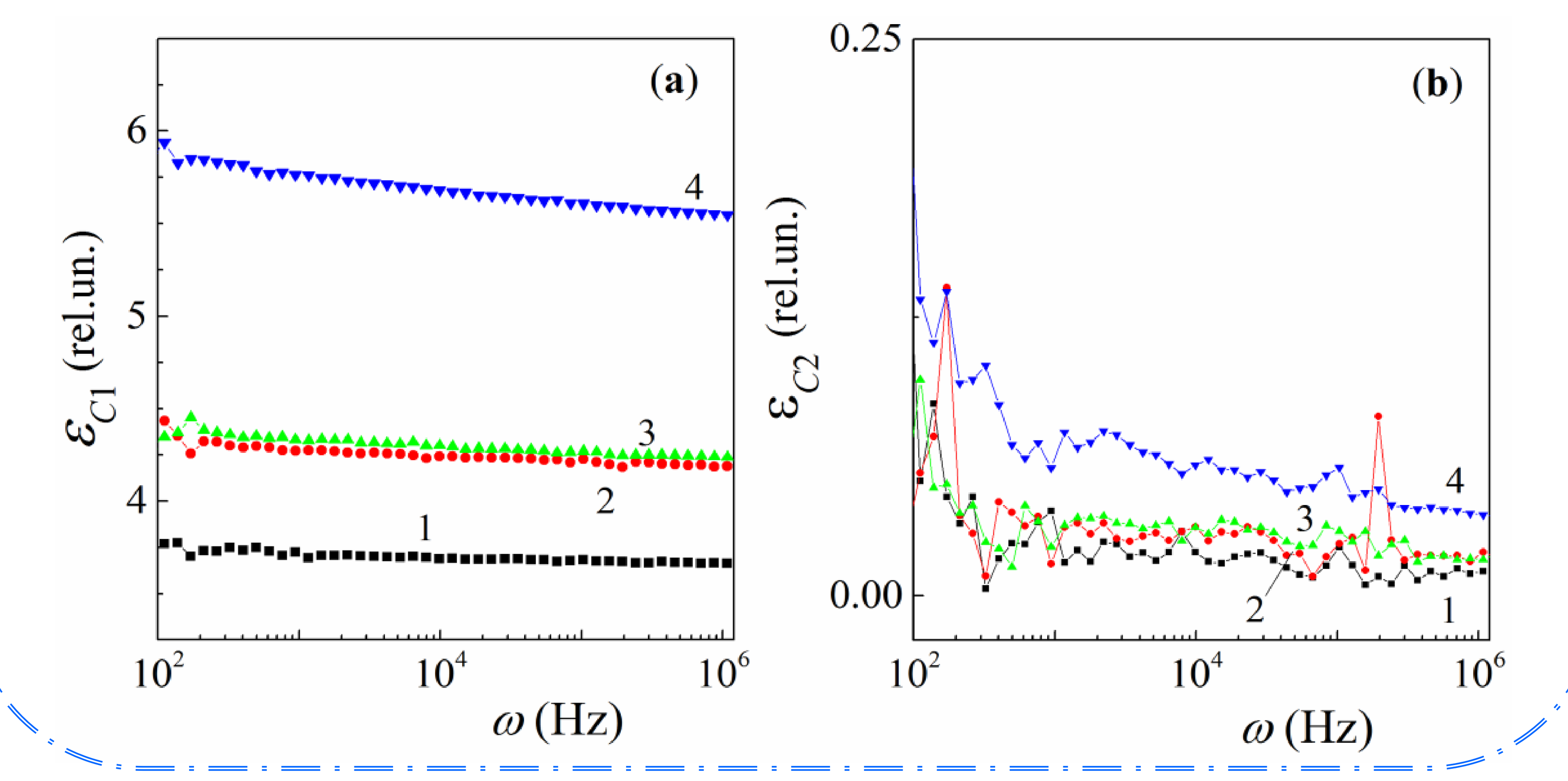
Estimation of the relative dielectric permittivity ε_{i1} (a) and the volume fraction φ_L (b) of the interphase layers versus the depolarization factor n for the MLG-filled epoxy nanocomposites at different loadings: φ_f=0.0053 (the curves "1"), φ_f=0.0107 (the curves "2"), φ_f=0.0271 (the curves "3")

ε_f = 15.0 + 0.2*j



The values depicted on the dependences $\varepsilon_{i2}(n)$ and $\varphi_i(n)$ are arithmetic-averaged for the frequency set $\omega/2\pi$ = [121.52Hz, 1026.3Hz, 10729Hz, 112160Hz, 1172500Hz]

Frequency dependences of relative dielectric permittivity ε_{C1} (a) and dielectric loss factor ε_{C2} (b) for the neat epoxy (the curves "1") and its composites with MLG-nanoplates measured at 95 K for different volume loadings: φ_f=0.0053 (the curves "2"), φ_f=0.0107 (the curves "3"), φ_f=0.0271 (the curves "4")



Conclusions

Variations in composite's dielectric permittivity with increasing the MLG-loading (φ_f) are nonmonotonous and can be explained by epoxy's molecular structure alteration in the interphase area.
An increasing of both the interphase's permittivity and the volume fraction with increasing φ_f evidences that the structure alteration is accompanied with breeding the dipole molecular fragments of the epoxy macromolecular chains.

References

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