ELECTRICAL PROPERTIES OF POLYMER COMPOSITES WITH FERROELECTRIC CERAMICS, CARBON FIBER AND METAL SALT

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Introduction

When polymeric materials serve for practical use, they are commonly mixed with other materials to achieve desired properties. For example, carbon-filled rubbers and fiber-reinforced plastics are mechanically improved polymer composites. Electrical properties can be broadly controlled by inorganic inclusions. For these composites, it has been a lasting key issue to predict the properties of composites properly using those of constituents. In this paper, we report on three types of polymer composites with ferroelectric ceramics, carbon nano-fiber and alkali-metal-salt which represent two phase systems consisting of independent, network forming and strongly interacting constituents. In these composites, dielectricity and conductivity are shown to be mutually correlated with each other through structural heterogeneity as revealed by broadband electrical spectra and predicted by appropriate mixing laws.

Ceramic powder/polymer composites

An introduction of ferroelectric ceramic powder imparts piezoelectric and pyroelectric activities as well as high dielectric permittivity. Such polymer composites can be modeled by a two-phase spherical dispersion whose physical properties have been expressed by a variety of mixing laws. One of the most successful is Bruggeman equation which relates the permittivity of the composite ε with that of constituents[1)]

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

Here subscripts 1 and 2 refer to matrix and spherical inclusion, respectively, and ϕ is the volume fraction of inclusions. When the constituents and composites are dielectrically lossy as well as conductive, their permittivity is given by a complex quantity

$$\varepsilon^*=\varepsilon'-i\varepsilon''+\frac{\sigma}{i\omega} \qquad (2)$$

Figure 1 shows the frequency spectra of complex permittivity and complex conductivity $\sigma^*=i\omega\varepsilon^*$ obtained for a composite consisting of barium titanate (BT) dispersed in $LiClO_4$–doped polyethylene oxide (Li-PEO). BT is a ferroelectric with large permittivity and Li-PEO is an ion conducting polymer. We find three dielectric and conductive processes at 1 GHz, 40 kHz and 4 Hz which are attributed to dielectric relaxation of PEO segments, interfacial polarization and electrode polarization, respectively. The observed spectra can be well reproduced by eq. (1) with the complex permittivities of the constituents.

In practice, we used BT fine particle samples with unknown permittivities and determined them as best-fit parameters that reproduced the observed spectra. We found that ε_2 decreases from 1970 to 360 as the diameter of BT powder decreases from 500 nm to 100 nm. It is known that BT assumes a cubic phase at the surface in contrast to the internal ferroelectric tetragonal phase, thus resulting in reduced permittivity in fine particles. Note that the use of ion conducting matrix is a key issue because the permittivity of BT is much larger than that of polymer matrix and so its value is insensitive to that of composite without interfacial polarization.

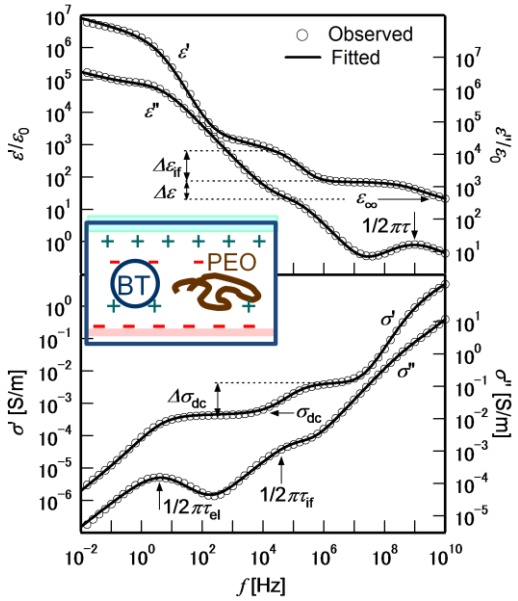

Fig. 1 Dielectric and conductive spectra for BT/Li-PEO composite

Carbon nanofiber/polymer composites

Polymer composites with carbon black, carbon naofiber (CNF) and carbon nanotube exhibit insulator-conductor transition associated with percolative conduction network formation. Figure 2

shows the frequency spectra of $\varepsilon'/\varepsilon_0$ and σ' for CNF/polyethylene (PE) composite with a CNF fraction ϕ ranging from 0.025 to 0.2. The rapid increase in dc conductivity σ_{dc} is accompanied by dielectric relaxation whose strength $\Delta\varepsilon$ becomes a maximum at percolation threshold near ϕ=0.1. We found that the details of the dielectric and conductive frequency spectra and the ϕ dependence of σ_{dc} and $\Delta\varepsilon$ are consistent with generalized effective medium approximation[2)]

$$(1-\phi)\frac{\varepsilon_1^{1/s}-\varepsilon^{1/s}}{\varepsilon_1^{1/s}+\left(\frac{1-\phi_c}{\phi_c}\right)\varepsilon^{1/s}}+\phi\frac{\varepsilon_2^{1/t}-\varepsilon^{1/t}}{\varepsilon_2^{1/t}+\left(\frac{1-\phi_c}{\phi_c}\right)\varepsilon^{1/t}}=0 \quad (3)$$

Accurate measurements of dielectric components in highly conductive sample at high frequencies allowed the observation of dielectric peaking predicted to occur at the percolation threshold.

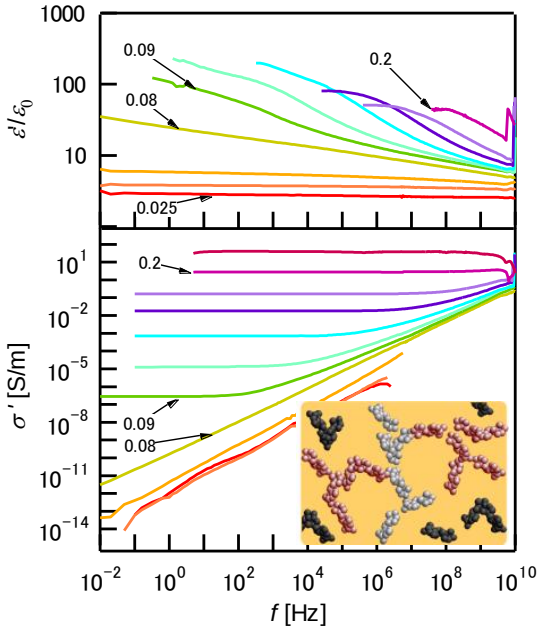

Fig. 2 Dielectric and conductive spectra for CNT/PE composites with varying CNF content.

Alkali metal salt/polyether composites

The alkali metal salt/polyether systems have attracted much interest because of their high ionic conductivity as well as intriguing conduction mechanisms[3)]. Polyethers are good solvents of various salts because ether oxygens tend to coordinate with cations. Dissociated ions acquire mobility with the aid of the microBrownian motion of polymer chains to achieve dc conduction.

Figure 3 show the frequency spectra of $\varepsilon'/\varepsilon_0$ and σ' for polyethylene oxide (PEO) composite with $LiClO_4$ As salt concentration Li/O is increased, σ_{dc} first increases and then start to decrease at a Li/O of 3%. The dielectric relaxation associated with the segmental motion of PEO molecules shifts toward the low frequency side. These results are indications of close correlation between ionic and molecular motions, i.e. cation coordination slows the segmental motion and slowed segmental motion impedes ionic diffusion. The diffusion coefficient is shown to be proportional to the relaxation frequency of slowed segmental motion with a proportionality coefficient being independent of salt concentration and temperature. The use of a random walk scheme revealed that ions hop at the same rate as segmental motion for a distance of monomer length.

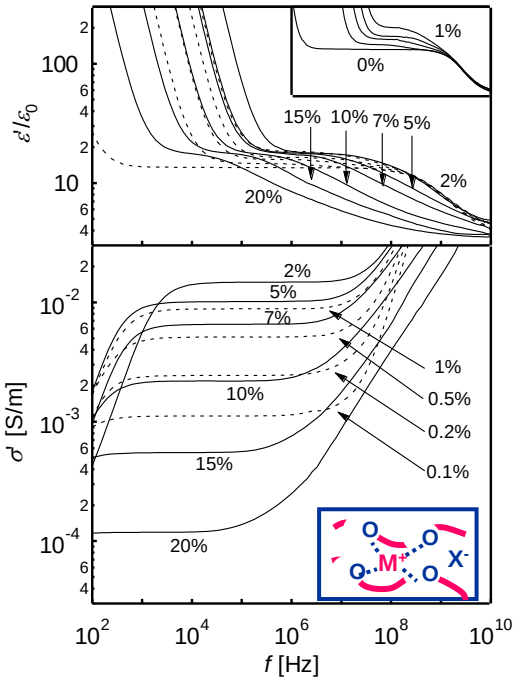

Fig. 2 Dielectric and conductive spectra for $LiClO_4$/PEO composites with a Li/O from 0.1% to 20%.

References

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