SHORT COMMUNICATION

Studies on the Polymers Having a High Dielectric Constant. VIII.[†] Blend Polymer Systems Consisting of a Monomeric—TCNQ Salt and Insulating Polymers

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Polymeric materials having a high dielectric constant and low dielectric loss are highly desired for the purpose of making film type capacitors small. Attempts made so far to meet this need have been mostly based on the orientation polarization of the side groups with large dipole moments, as is exemplified by such polymers as cyanoethylated cellulose¹ and poly(vinylidene fluoride).² The dielectric constant of 10—15 was the maximum in these polymers.

In order to attain a higher ϵ_r , we have been investigating a new approach³ based on a polarization process other than the orientation polarization, *i.e.*, interfacial polarization. An electrically conductive component is microscopically dispersed in an insulating polymer component, and the interfacial polarization induced by the migration of electronic carriers in the dispersed conductive phases is expected to be effective in these systems. We wish to report in this paper that we were able to succeed in preparing a polymer blend system having relatively high ϵ_r , ~ 100 , in commercial frequency region with a relatively low $\tan \delta$ value, being about 3%, by dispersing a highly conductive *n*-butylquinolinium—TCNQ (tetra-

cycanoquinodimethane) complex salt in nonconducting polymers such as polystyrene and polysulfone.

The preparation of these blend polymers will be described later. The electrical properties of the blend polymers are summarized in Table I and Figures 1 and 2. Table I shows specific resistivities at room temperature. As shown in the table, the blend polymers containing more than 10 wt % of the complex salt have a somewhat lower resistivity and are considered no longer suitable as dielectric material. Figure 1 shows the frequency dependence of ϵ_r and $\tan \delta$ at room temperature for the blend polymers of the polystyrene matrix. As shown in the figure, the value of ϵ_r in the low frequency region (< 1 kHz) is high ($\epsilon_r > 30$) and increases with greater concentration of the complex salt. However, ϵ_r decreases in a high frequency region, and $\tan \delta$ maximum appears at 10—40 kHz. In contrast to the blend polymers with the complex salt, the value of ϵ_r of the blend polymer with a simple salt ($\square$ in Figure 1) is very low and nearly equal to the value of just the polystyrene. In Figure 2, ϵ_r and $\tan \delta$ values for the blend polymers of the polysulfone matrix are plotted against frequency. The dielectric behavior of these blend polymers is similar to the case of the polystyrene matrix, *i.e.*, ϵ_r in low frequency region below 110 Hz is high and increases with the complex salt concentration up to 10 wt %. However, ϵ_r decreases when the content of the complex salt becomes 20 wt %. $\tan \delta$ maximum also appears at 2—5 kHz for the

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Table I. Specific resistivities ρ of blend polymers at room temperature, and the shape factor n and specific resistivities ρ_2 of the conductive phase in the blend polymers calculated by Sillars theory

Sample	Insulating polymer	Complex salt ^a content (wt %)	$\rho, RT, \Omega\text{cm}^b$	n^c	a/b^d	$\rho_2, \Omega\text{cm}$	f_m, Hz^e	ϵ_{r0}^f
I	Polystyrene	2.5	10^{11}	431	38	6.4×10^4	2.5×10^4	32
II	Polystyrene	5.0	10^{11}	531	43	8.1×10^4	1.6×10^4	73
III	Polystyrene	10.0	10^8	808	55	3.9×10^4	2.2×10^4	214
IV	Polysulfone	5.0	10^{13}	368	35	7.8×10^5	2.0×10^3	62
V	Polysulfone	10.0	10^8	823	55	1.6×10^5	4.5×10^3	260
VI	Polysulfone	20.0	10^6	—	—	—	—	—

^a *n*-Butylquinolinium—TCNQ complex salt. Multiplication of this content (wt %) by a factor of 0.69 gives the TCNQ content (wt %) of the blend polymer. Specific resistivities of the simple and complex salts at room temperature are 6.0×10^8 and $8.8 \times 10^8 \Omega\text{cm}$, respectively, from compressed powder measurements.

^b Resistivities are dependent to some extent on applied voltage. Values are given to illustrate the order of resistivity.

^c Shape factor of the conductive phase calculated by eq 3.

^d Ratio of major and minor axes of ellipsoid of rotation.

^e Determined by the data of frequency dependence of $\tan \delta$ as plotted in Figures 1 and 2.

^f Low frequency relative dielectric constant of blend polymers.

Figure 1. Plots of dielectric constant, ϵ_r and $\tan \delta$ vs. frequency for blend polymers of the polystyrene matrix at room temperature: (●), sample I; (△), sample II; (○), sample III; (□), blend polymer with simple salt (6.7 wt %), TCNQ content is nearly equal to that of sample II.

Figure 2. Plots of ϵ_r and $\tan \delta$ vs. frequency for blend polymers of polysulfone matrix at room temperature: (△), sample IV; (○), sample V; (□), sample VI.

blend polymers of the polysulfone matrix and the relaxation frequencies f_m at which $\tan \delta$ maximum appears are lower by about one order of magnitude than that of the blend polymers of the polystyrene matrix.

According to the theory⁴ of heterogeneous dielectrics in which conducting particles (2), having

rotation ellipsoid shapes, are dispersed in an insulating matrix (1), the relaxation time τ and the relaxation strength k are expressed by

$$\tau = \frac{1}{2\pi f_m} = \frac{(n-1)\epsilon_0\epsilon_{x1} + \epsilon_0\epsilon_{x2}}{\sigma_2} \quad (1)$$

$$k = \frac{\epsilon_{x0} - \epsilon_{x\infty}}{\epsilon_{x1}} = n^2 q \frac{\epsilon_{x1}}{(n-1)\epsilon_{x1} + \epsilon_{x2}} \quad (2)$$

where ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.855 \times 10^{-12}$ F/m), σ is the conductivity, ϵ_{x1} and ϵ_{x2} are relative dielectric constants of insulating matrix and conducting particles, ϵ_{x0} and $\epsilon_{x\infty}$ are the low and high frequency relative dielectric constants of heterogeneous dielectrics, q is the volume fraction of conducting particles, and n is the shape factor of conducting particles, and is calculated by

$$n = \frac{2}{ab^2} \left[\int_0^\infty \frac{du}{(a^2+u)(b^2+u)\sqrt{a^2+u}} \right]^{-1} \quad (3)$$

where a and b are major and minor axes of ellipsoids of rotation. Owing to low conductivities of the insulating matrix, σ_1 is omitted in eq 1 and 2.

As the blend polymers may be considered as heterogeneous dielectrics in which conductive phases, consisting of the complex salt, are microscopically dispersed in the insulating polymer matrix, the dielectric behavior observed in blend polymers can be analyzed by this theory. The parameter values for calculation have been chosen as the following: ϵ_{x1} and $\epsilon_{x\infty}$ are 2.6 and 4.0 in the case of polystyrene matrix, and 3.1 and 5.0 in the case of polysulfone matrix, and ϵ_{x2} is 10. The results are tabulated in Table I along with the values of other parameters used for calculation. For the calculation of n in eq 2, the volume fraction of the conductive phase is assumed to be equal to the weight fraction. All of the values chosen for calculation are considered reasonable. Change in parameter values within a conceivable range, and the assumption regarding the fraction of the conductive phase do not alter the calculated result so much.

As clearly shown in the table, (1) the shape of the conductive phase is slender and becomes more so with an increase in the fraction of conductive component; (2) the specific resistivity of the conductive phase is higher than that of the pure complex salt; (3) the specific resistivity of the conductive phase in polysulfone matrix seems to be higher

than that in the polystyrene matrix. This (1) is conceivable, since the complex salt tends to be separated in needle like crystals from the solution. It is probable that the crystal structure of the pure complex salt might be destroyed or deformed in the polymer matrix. This deformation of crystal structure leads to a lowering of the conductivity of the conductive phase in the polymer matrix. The reason for this may be attributed to (2). Owing to the nonpolar nature of polystyrene, the complex salt is expected to have a poorer compatibility with polystyrene than with polysulfone; and thus, the crystalline structure of the complex salt is destroyed or deformed less in the polystyrene matrix than in the polysulfone matrix. This may be explained by (3). For further discussion, the information on the microscopic structure of blend polymers is necessary.

Nevertheless, if we could find the blend polymer in which the complex salt is able to keep its inherent high conductivity even in polymer matrix, we should be able to expect a material having high ϵ_r and low $\tan \delta$ up to high frequency region. The blending of various kinds of highly conducting TCNQ salts with different kinds of insulating polymers should be investigated.

Experimental details are as follows:—*n*-Butylquinolinium—TCNQ (simple salt) was prepared by reacting the corresponding iodide and LiTCNQ, using the method in the literature.⁵ Complex salt was prepared by reacting an equimolar amount of simple salt and neutral TCNQ molecule. The decomposition temperatures of the simple and complex salts were 154°C and 203°C, respectively. Identification of both salts was carried out by elemental analyses, infrared and visible spectra, and were consistent with the expected structures. Reagent grade polystyrene was purified by precipitation. Polysulfone (Union Carbide Corp. P-1700) was used as received. Blend polymer films were prepared by mixing a weighed amount of complex salt and insulating polymers in purified DMF (dimethyl formamide), and casting the clear solution onto a glass plate and evaporating the solvent under vacuum. As the solvent evaporates, the transparent greenish solution becomes dark and opaque. Crystals separated macroscopically could not be seen on the film. In order to eliminate the remaining solvent thoroughly, films were dried further for 30 hr at 95°C in 10^{-2} torr. The thick-

ness of the films was 100–200 μm . Gold was evaporated onto the films to form a three terminal electrode. Measurements of the electrical properties were carried out under a vacuum of 10^{-2} torr, using a three terminal guarded electrode cell⁶, in a manner similar to that described previously.⁷

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