Effect of interphase interactions on the dielectric behaviour of polycarbonate/poly(styrene-*co*-acrylonitrile) blends

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Summary

Frequency and temperature dependences of the complex permittivity $\varepsilon^*(= \varepsilon'- i \varepsilon''$, ε' is the real and ε'' imaginary component, respectively) were investigated for blends of polycarbonate/poly(styrene-*co*-acrylonitrile) (PC/SAN). In the blends, two α-processes corresponding to the main transitions of PC and SAN were found; for SAN at concentrations $c_{SAN} \geq 20$ wt% and for PC for $c_{PC} \geq 40$ wt%. The Havriliak-Negami shape parameters describing the frequency dependence of ε' and ε'' are virtually independent of temperature and composition. Slight shift of temperature or frequency positions of α-processes found for blends from those found for neat polymers with composition of blends indicated partial miscibility of components. The concentration dependences of ε' and ε'' at low frequencies and high temperatures could be described with the Böttcher equation from which it followed that percolation threshold takes place for SAN inclusions at $c_{SAN} \approx 30$ wt%. Both the reduced dielectric strength $\Delta\varepsilon T$ and the reduced Onsager term O_t/c_{SAN} (or O_t/c_{PC}) in dependence on the blend composition could be qualitatively described by the Böttcher equation as well.

Introduction

The main incentive for two-phase polymer blend preparation is the fact that heterogeneous materials are superior to homogeneous ones as far as mechanical properties are concerned (1,2). A main problem of heterogeneous blends is the interfacial adhesion which has to be strong enough to transmit acting stress up to the yield or tensile strength. Partial miscibility is one of the ways of achieving this situation. Polycarbonate (PC) has attracted much attention because of its outstanding mechanical properties and many binary blends of PC with polar polymers, such as poly(styrene-*co*-acrylonitrile) (SAN), poly(methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) were investigated (3-7). In general, these systems consist of two conjugate phases, the P_1-rich and P_2-rich, which contain a low percentage of the other component. In the conjugate phases the molecular environment differs from that in homopolymers and one can expect that the motion of molecules will be influenced by interactions between the blend components.

To study the molecular dynamics in polymers and blends, dielectric spectroscopy was used for investigation of PC (6) and of blends of PC with tetramethyl-Bisphenol A polycarbonate (TMBPA-PC) (7). While several dispersion regions were found in PC, only one broadened α-relaxation was detected in its blends with TMBPA-PC. In blends of PC/SAN, two glass transitions were found in the DSC thermograms (8) indicating that blends consist of two phases formed by PC and SAN components. A broadening of DSC peak (shown by dependence of the specific heat $c_p(T)$ on temperature) in the PC transition region with blends composition was detected, while practically no DSC changes in the zone of SAN transition were found. The dielectric measurements showed no significant differences between the blends and the neat SAN copolymer; the main transition region of PC blends was not analysed due to a small polar activity of PC.

In this work we investigate the dielectric behaviour of blends of PC/SAN in a broad frequency and temperature region. Main attention is devoted to the effect of miscibility and interphase interactions on the shape and position of dielectric functions in dependence on temperature and frequency.

Experimental

Sample preparation. Bisphenol A polycarbonate SINVET 251 (ENI, PC; density $\rho = 1.20$ g cm^{-3}, $M_n = 25\ 000$, $M_w = 36\ 000$) and poly(styrene-*co*-acrylonitrile) KOSTIL AF 600 (ENI, SAN; 24 wt.% AN, $\rho = 1.07$ g cm^{-3}, $M_n = 69\ 500$, $M_w = 135\ 000$) were used for PC/SAN binary blends preparation. Polymers were premixed in a slow-rotating mixer and fed into a twin-screw extruder hopper through a gravimetric feeder (feeding rate ~ 20 kg/h). The screw profile and temperature regime were optimized to achieve good mixing without SAN degradation (at ~ 220 °C). Samples were prepared by injection molding; the barrel and mold temperatures were set to 210 and 60 °C, respectively. The composition of samples was: PC/SAN = 100/0, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, and 0/100 by weight.

Dielectric measurements. Dependences of the complex permittivity $\varepsilon^* = \varepsilon' - i\ \varepsilon''$ (ε' is the storage and ε'' is the loss component) on frequency $f = 1/(2\pi\omega)$ (ω is the angular rate) and temperature T were measured by a Hewlett-Packard 4192A LF Impedance Analyzer in the frequency range from 5 Hz to 13 MHz and in the temperature interval from 20 to 220 °C. All samples were melted and placed between stainless steel electrodes. To keep the thickness of the samples constant, the glassy fibers (50 μm in diameter) were used as a spacer. To provide the same thermal history, all samples were annealed for 2 h at 180 °C and then, before measurements, cooled down to 20 °C at a cooling rate of 0.5 °C/min. The measurements were carried out at various constant temperatures in the regime of increasing temperature. The sample was equilibrated at a given temperature for ~ 15 min and a frequency scan was measured; then, temperature was increased by 3-5 °C and the whole procedure was repeated. For PC, the regime of decreasing temperature was also used.

The dielectric data were described as a superposition of two terms

$$\varepsilon^* = \varepsilon_d^* + \varepsilon_c^* \tag{1}$$

The first (dispersion) term was represented by the Havriliak-Negami equation (9)

$$\varepsilon_d^*(\omega) = \varepsilon'_\infty + \Delta\varepsilon/[1 + (i\omega\tau)^b]^c \tag{2}$$

where $\Delta\varepsilon = \varepsilon'_o - \varepsilon'_\infty$ is the dielectric strength, ε'_o and ε'_∞ being the relaxed ($\omega = 0$) and unrelaxed ($\omega = \infty$) values, $\tau = 1/(2\pi f_r)$ is the relaxation time, and b and c are the shape parameters of the relaxation time distribution function. The parameter f_r is related to the peak frequency f_m (at which ε'' attains its maximum value) by $(f_m/f_r)^b = \sin \gamma/\sin (c\gamma)$, where $\gamma = (b\pi/2)/(1 + c)$.

For the second (conductivity) term we used the expression (10)

$$\varepsilon_c^* = C\ (if_c/f)^d \tag{3}$$

where f_c and C are constants. Usually the value of d slightly differs from unity, which means that conductivity has, at least partly, some relaxation character. A computer program was developed (10) for fitting the experimental data with Eq. (1); the program is based on the Marquardt fitting procedure (11).

Results and discussion

Temperature dependences. In accord with the literature (6), three dispersion regions were observed for PC in dependence of ε'' on T in the interval from 20 to 220 °C. The broad, low-temperature β-process (located at temperatures from 20 to 100 °C) corresponds to
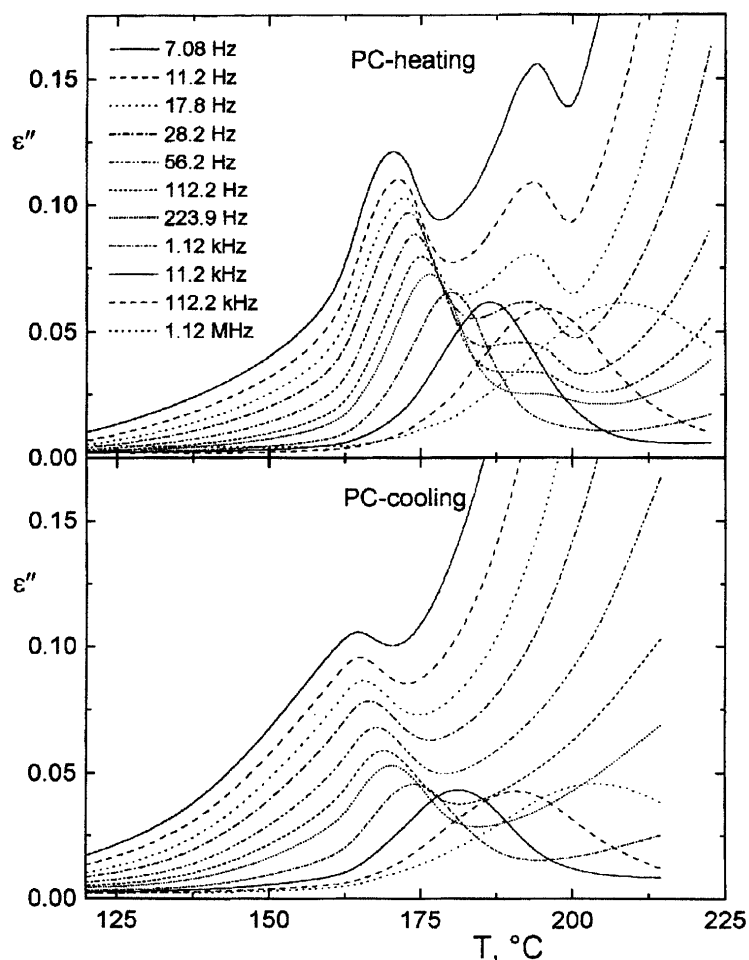
Figure 1. Temperature dependences of the loss permittivity ε'', for polycarbonate at selected frequencies

the local motion of the carbonyl groups (6,7). In Fig. 1 (data shown in the interval from 120 to 220 °C), the loss peak (located at $T > 150°$) in the $\varepsilon'' - T$ dependence is clearly seen; this dispersion can be attributed to the primary (α-process) relaxation associated with the cooperative motion of PC chains in the glass transition region. The height of the maximum decreases with increasing frequency and the peak shifts to higher temperatures. The third peak (α'-process), located at temperatures above the α-process in the heating regime, can be attributed to a Maxwell-Wagner-Sillars (MWS) polarization arising from the interfaces between ordered and disordered domains in PC (6). While its intensity strongly depends on frequency, the temperature position of the peak seems to be frequency-independent. It is interesting to note that in the subsequent cooling regime from 220 °C, the α'-process is missing and only one α-dispersion region can be observed in Fig. 1. This means that the formation of ordered regions requires time which was not sufficient in cooling experiments. For most frequencies at highest temperatures, the conductivity contribution in ε''-T dependences can be seen. In Fig. 1 it can be also seen that the presence of α'-process in the heating run slightly shifts the ε''-T maximum of α-process to higher temperatures and leads to a lower conductivity contribution at highest temperatures in comparison with the cooling run.

An example of measured temperature dependences of the loss permittivity ε'' at various frequencies f for blends is shown in Fig. 2 for sample 80/20 in the temperature interval 120-220°C. While for $f = 11$ Hz, only α-relaxation of SAN and dc conductivity is found, for $f = 1.1$ kHz, both α-processes for SAN and PC are observed; for $f \geq 110$ kHz, both relaxations overlap and only one broad peak in ε''-T dependence is seen. Qualitatively
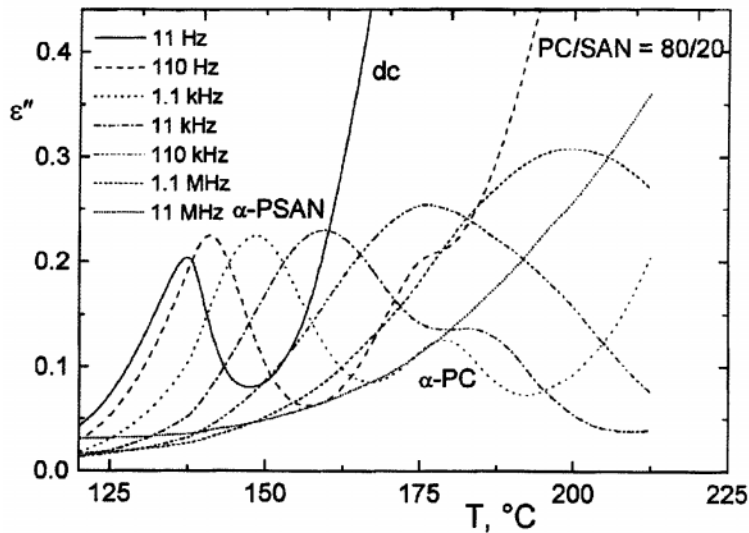
Figure 2. An example of temperature dependence of the loss permittivity ε'', for PC/SAN = 80/20 blend.

similar results were obtained for other blends. Neat SAN shows the simplest behaviour in the dependence of ε'' on T, with only one α-peak and conductivity contribution (ε'' on T curves exhibit the shape similar to curve shown in Fig. 2 and measured at 11 Hz).

Frequency dependences. An example of the used decomposition procedure for fitting experimental data is shown in Fig. 3 where the ε'' vs. f dependence measured at 178.8 °C for the 80/20 blend is given. Both α-processes related to homopolymers together with the conductivity contribution were extracted from the data. Similar results were obtained for most blends. In such a way the parameters of Eqs (2) and (3) - the peak frequency f_m, the reduced dielectric strength $\Delta\varepsilon T$, shape parameters b and c, and conductivity exponent d - could be determined for α-dispersion of homopolymers and corresponding α-processes in blends. Due to polar nitrile groups in SAN, the reduced dielectric strength of SAN ($\Delta\varepsilon T \sim 4000$ K) is much higher than that of PC ($\Delta\varepsilon T \sim 140$ K). In accord with this fact, the strong α-relaxation associated with the SAN component could be detected in blends at all SAN concentrations; the α-process corresponding to PC component could be found only for concentrations $c_{PC} \geq 40$ wt.%.

The temperature dependences of the peak frequencies f_m of neat polymers and blends are shown in Fig. 4. In all cases these dependences obey the WLF equation in the form (1)

$$\log (f_m/f_s) = -8.86 (T - T_s)/(101.6 + T - T_s) \tag{4}$$

where T_s is the reference temperature and f_s is the f_m value at T_s. For SAN, $\log f_s = 3.6$ (Hz), $T_s = 150.4$ °C and for PS, $\log f_s = 5.6$ (Hz) and $T_s = 201.8$ °C. The temperature dependences of f_m of both α-relaxations found in blends lie between those in the neat polymers (Fig. 4). Similarly enough, a slight decrease in T_s values corresponding to the α-process of PC and a slight increase in T_s values related to the α-process of SAN is
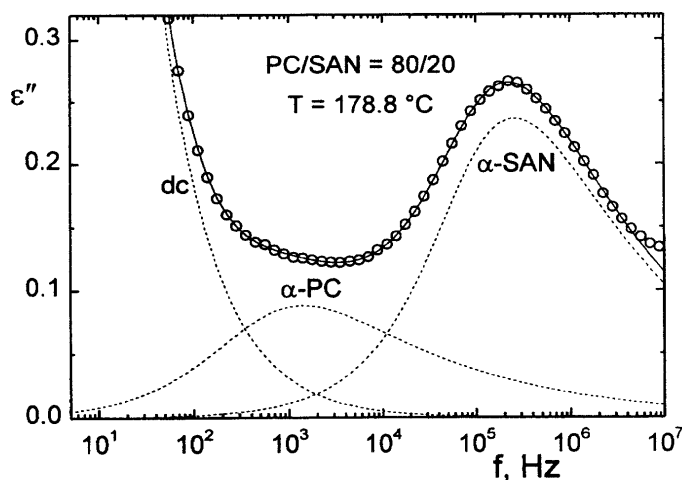

Figure 3. An example of decomposition of the frequency dependence of the loss component ε'', measured at 178.8 °C (Eqs (2) and (3)) for PC/SAN = 80/20 blend: ○ experiment, —— $\varepsilon^*_d + \varepsilon^*_c$.
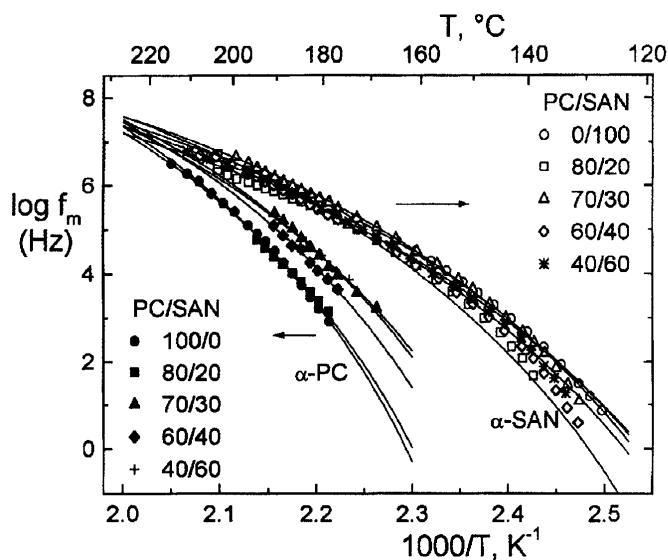
Figure 4. Temperature dependences of the peak frequencies f_m, for neat polymers and blends.

found for blends with decreasing contents of the corresponding component (Fig. 5). The reason for these findings is that a small fraction of PC (or SAN) dissolved in SAN (or PC) accounts for a small increase (or decrease) in T_s temperature of the SAN (or PC) phase. This fact confirms a partial miscibility of components in our blends

In all cases, the shape of α-relaxations is asymmetric; we have found that the HN shape parameters b and c are virtually independent of temperature (for SAN $b \sim 0.8$ and $c \sim 0.5$, and for PC $b \sim 0.7$ and $c \sim 0.4$). The shape parameters of both α-processes in blends correspond to those of neat polymers. An exception was found only for blend 20/80 with the lowest PC content where only SAN α-relaxation was fitted by Eq. (2); in this case significant deviations ($b \sim 0.65$ and $c \sim 0.4$) were found for SAN shape parameters. This means that the shape parameters are not much sensitive to partial miscibility of phases.

For samples, the value $d \approx 0.9 - 1$ was found regardless of the blend composition, and the temperature dependence of the conductivity could be represented by the Arrhenius equation with average activation energy $\Delta U \approx 1.3 \pm 0.1$ eV. From the fitting parameter C (Eq. (3)), the values of reduced conductivity $\sigma_{10}/\varepsilon_o$ (σ_{10} is related to $f = 10$ Hz and ε_o is the permittivity of vacuum) were evaluated at $T = 203$ °C and plotted in Fig. 5 in dependence on the SAN concentration. The break observed in this dependence suggests that the continuous SAN phase is formed in the region with $c_{SAN} \geq 20$ wt.%. It was also found that the conductivity of PC homopolymer is about three orders of magnitude lower than that of SAN.

Effect of blend composition. To predict the dielectric behaviour of polymer blends, one must know not only the properties of individual components and their volume fractions, but also the geometrical arrangement of phases and their interactions as well. A number of relationships have been published (1,13,14). For quantitative analysis, we have used an equation originally suggested by Böttcher (15) which was later on modified for ellipsoidal shape of immersed particles (component 2) and has the form (16,17)

$$\frac{(\varepsilon_1{}^* - \varepsilon^*)\, v_1}{\varepsilon^* + (\varepsilon_1{}^* - \varepsilon^*)\, A} + \frac{(\varepsilon_2{}^* - \varepsilon^*)\, v_2}{\varepsilon^* + (\varepsilon_2{}^* - \varepsilon^*)\, A} = 0 \tag{5}$$

where ε^*, $\varepsilon_1{}^*$ and $\varepsilon_2{}^*$ are the permittivities of the blend, component 1 and component 2, respectively, v_2 and v_1 are the volume fractions of the respective components ($v_1 = 1 - v_2$) and A is the depolarization factor of the immersed particles along the axis parallel to electric field (the spherical geometry assumes the value of $A = 1/3$). Equation (5) predicts the percolation threshold for $v_{2c} = A$ (for for $v_2 \geq v_{2c}$ phase 2 is continuous).
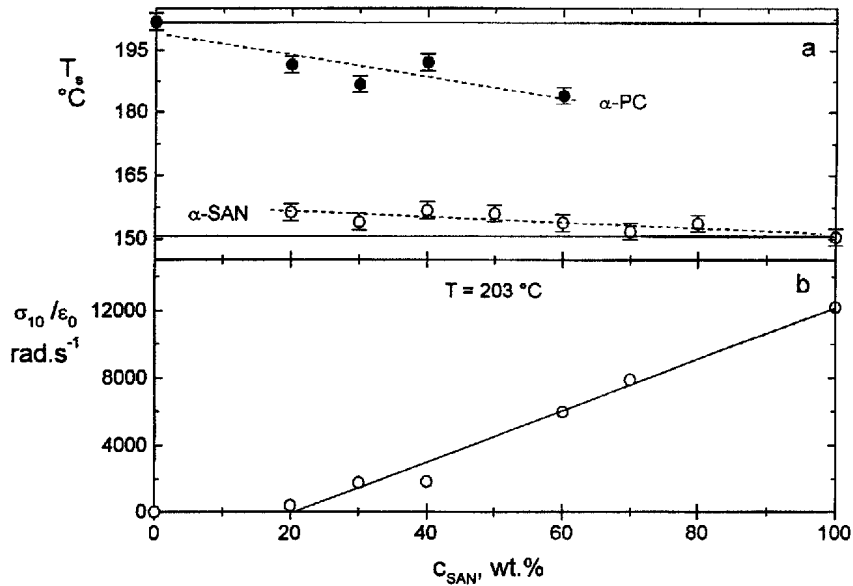
Figure 5. Concentration dependences: (a) the reference temperature T_S (Eq.(4)), related to α-SAN process ($\circ$) and α-PC process ($\bullet$); (b) the reduced conductivity $\sigma_{10}/\varepsilon_o$ related to 203 °C ($\circ$).
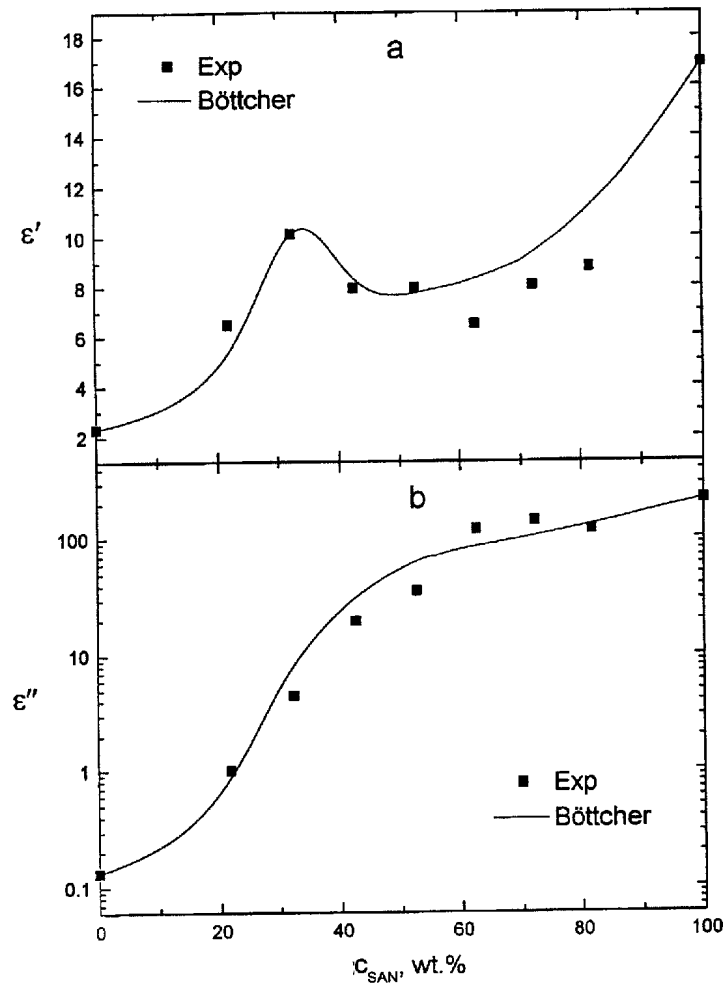
Figure 6. Concentration dependence of the storage ε' (a) and of the loss ε'' (b) permittivity measured at f = 11.2 Hz and T = 207 °C; $\blacksquare$ experiment, ——— Böttcher equation (Eq. (5)).

Figure 6 shows the concentration dependence of storage ε' and loss ε'' components of permittivity at low frequency f=11.2 Hz and temperature T=207°C. It can be seen that the Böttcher equation (Eq. (5)) with the value of $A = 1/3$ roughly describes the data; this means that the percolation threshold is achieved at v_{2c}=1/3 (c_{SAN}~0.3).

The reduced dielectric strength $\Delta\varepsilon T$ of both α-processes was found to be temperature-independent for all samples. Due to the presence of polar nitrile groups in SAN, the $\Delta\varepsilon T$ value is much higher (3750 K) than that of PC (133 K). As follows from Fig. 7, the $\Delta\varepsilon T$ values of individual α-processes decrease with decreasing content of corresponding component in blends. It is interesting to note that the Böttcher equation describes experimental data at least in the first approximation.
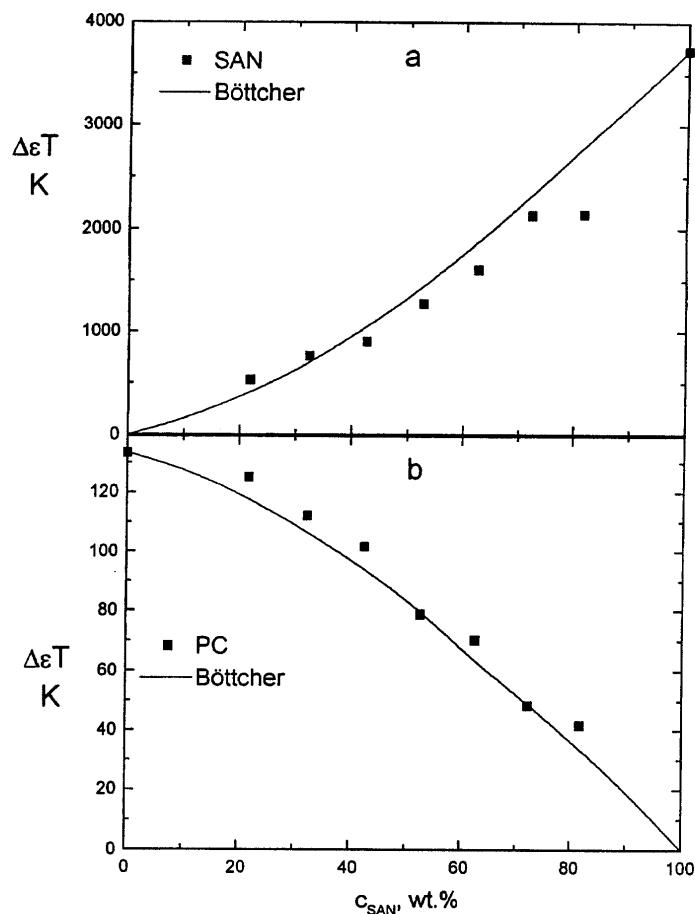

Figure 7. Concentration dependence of the reduced dielectric strength $\Delta\varepsilon T$ of the α-process of SAN (a) of PC (b); ■ experiment, —— Böttcher equation (Eq. (5)).

If we assume the matrix-immersed particles type of the two-phase structure, the square dipole moments per monomer unit of SAN and PC can be calculated from ε'_o and ε'_∞ corresponding to individual α-relaxations using the Onsager equation in the form (18)

$$\mu^2 = 9\,\varepsilon_o kT\,(\varepsilon'_o - \varepsilon'_\infty)/[N\varepsilon'_o(\varepsilon'_o + 2)^2] \tag{6}$$

where k is Boltzmann constant and N is number of monomer units per unit volume. For further analysis, we calculated the values of the Onsager terms $O_t = (\varepsilon'_o - \varepsilon'_\infty)$ $T/[\varepsilon'_o(\varepsilon'_\infty + 2)^2]$, which are proportional to $N\mu^2$. In Fig. 8 the reduced Onsager terms O_t/c_{SAN} and O_t/c_{PC}, which are proportional to μ^2, are plotted in dependence on the composition of blends. Surprisingly, the O_t/c_{SAN} value of SAN (~ 10 K) is only three times larger than that of PC (~ 3.3 K). While the introduction of the nonpolar PC component into blends generally leads to an increase in O_t/c_{SAN} values corresponding to the SAN component, the introduction of a highly polar SAN component to blends leads to a decrease in O_t/c_{PC} values of PC component. Also in this case, both concentration dependences can be qualitatively described by the Böttcher equation (Eq. (5)).
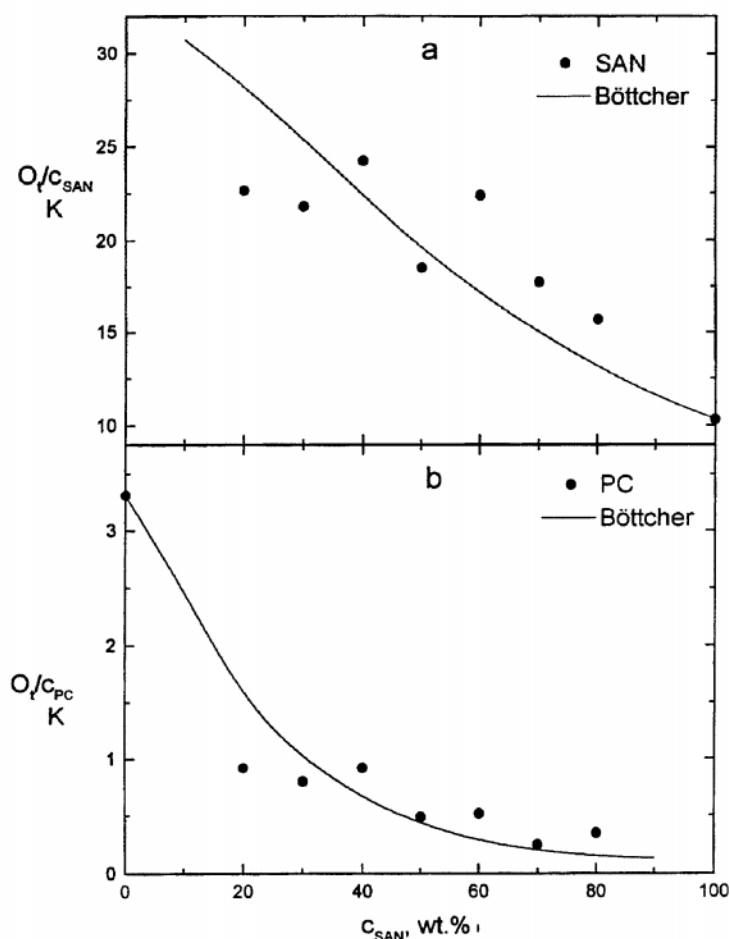
Figure 8. Concentration dependence of the reduced Onsager term O_t/c_{SAN} ($\sim O_t/N \sim \mu^2$) of the α-process of SAN (a) and O_t/c_{PC} term of PC (b); ● experiment, —— Bőttcher equation (Eq. (5)).

Acknowledgement

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