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Dielectric Behaviour of Polycarbonate/Poly(styrene-*co*-acrylonitrile) and Polycarbonate/Poly(methyl methacrylate) Two-Phase Blends

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Summary: Frequency and temperature dependencies of the complex permittivity ε^* were investigated for two-phase blends polycarbonate/poly(styrene-*co*-acrylonitrile) (PC/SAN) and PC/poly(methyl methacrylate). The frequency dependencies of the ε^* at all temperatures were described by the Havriliak-Negami (HN) equation and the conductivity contribution. The effect of mutual miscibility on the HN shape parameters and temperature dependencies of the peak frequences f_m (at which loss component ε'' attains its maximum value) is discussed. The Böttcher equation is used for describing the effect of the blend composition on the reduced dielectric strength $\Delta\varepsilon T$, the dipole moment μ and ε^* values measured at the highest temperatures (in the conductivity region). The role of Maxwell-Wagner-Sillars polarization due to interfaces between ordered and disordered domains in PC is mentioned.

Introduction

Two-phase polymer blends have found widespread applications as their ultimate properties are superior to homogeneous blends[1,2)]. A major problem of these blends is the interfacial adhesion which has to be sufficient to transmit acting stress; partial miscibility is one of the ways of achieving this situation. Polycarbonate (PC) has attracted much attention and many binary blends of PC with polar polymers were investigated[3-7)]. In general, these systems consist of two conjugate phases, which contain a low percentage of the other component. In the conjugate phases molecular environment differs from that in neat polymers and one can expect that the motion of molecules will be influenced by interactions between the blend components.

To study the molecular dynamics, the dielectric spectroscopy was used for investigation of PC[6)] and of blends of PC with tetramethyl-Bisphenol A polycarbonate (TMBPA-PC)[7)].

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While several dispersion regions were found in PC, only one broadened α-relaxation was detected in its blends with TMBPA-PC. In blends PC/SAN, two glass transitions were found in DSC thermograms8) indicating that blends consist of two phases identical with PC and SAN components. At the same time the dielectric measurements8) showed no significant differences in the SAN behavior between the blends and the neat SAN copolymer; the main transition region of PC blends was not analysed due to a small polarity of PC.

It was stated that blends of PC/PMMA exhibit a lower critical solution temperature above 200 °C and therefore can be prepared with single-phase or two-phase structure9,10). The one-phase blends are usually prepared by casting films from THF solution and subsequently drying under vacuum at 110 °C. Annealing of such blends between 200 and 250 °C for several hours did give an opaque film with two glass transitions10) so that two-phase structure is a stable state of blends. Using dynamic mechanical spectroscopy, suppression of the secondary β-relaxation of PMMA by addition of PC was found in two-phase PC/PMMA blends10).

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

Experimental

Sample preparation. Both series of PC/SAN and PC/PMMA blends with two-phase structure were prepared using the same procedure. Bisphenol A polycarbonate (PC) SINVET 251 (ENI; ρ = 1.20 g cm^{-3}, M_n = 25 000, M_w = 36 000) and poly(styrene-*co*-acrylonitrile) (SAN) KOSTIL AF 600 (ENI; 24 wt-% AN, ρ = 1.07 g cm^{-3}, M_n = 69 500, M_w = 135 000) were used for PC/SAN blends preparation. Poly(methyl methacrylate) (PMMA) VEDRIL 90 (ENI; ρ = 1.19 g cm^{-3}, M_n = 68 000, M_w = 100 000) was used in PC/PMMA blends. Speciments were prepared by injection molding; the barrel and mold temperatures were set to 210 and 60 °C, respectively. The composition of blends was: PC/SAN = 100/0, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 0/100 and PC/PMMA = 95/5, 90/10, 85/15, 80/20, 70/30, 60/40, and 0/100 by weight.

Dielectric measurements. Dependencies 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 5 Hz – 13 MHz and in the temperature interval 20–220 °C. To keep the thickness of the samples constant, the glass fibers (50 μm in diameter) were used as a spacer. The samples were annealed for 2 h at 180 °C and then cooled down to 20 °C at a cooling rate of 0.5 °C/min. The measurements were carried out at selected constant temperatures in the regime of increasing temperature. The sample was equilibrated at a given temperature for ~ 15 min before a frequency scan was initiated; afterwards, 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$^{11)}$

$$\varepsilon^* = \varepsilon^*_d + \varepsilon^*_c \qquad (1)$$

The first term was represented by the Havriliak-Negami (HN) equation$^{12)}$

$$\varepsilon^*_d(\omega) = \varepsilon'_\infty + \Delta\varepsilon/[1 + (i\omega\tau)^b]^c \qquad (2)$$

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 of storage component, $\tau = 1/(2\pi f_r)$ 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$^{11)}$

$$\varepsilon^*_c = C\,(if_c/f)^d \qquad (3)$$

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, based on the Marquardt fitting procedure$^{13)}$, was developed$^{12)}$ for fitting the experimental data with Eq. (1)–(3).

Analysis of blend composition. A number of relationships have been published[1,14-16] to predict the dielectric behavior of a heterogeneous blend from the knowledge of its composition and of properties of neat components. For quantitative analysis, we will use an equation originally suggested by Böttcher[17] which was later modified for ellipsoidal shape of immersed particles (component 2)[18,19]

$$\frac{(\varepsilon_1^*-\varepsilon^*)\,v_1}{\varepsilon^*+(\varepsilon_1^*-\varepsilon^*)\,A}+\frac{(\varepsilon_2^*-\varepsilon^*)\,v_2}{\varepsilon^*+(\varepsilon_2^*-\varepsilon^*)\,A}=0 \tag{4}$$

where ε^*, ε_1^* and ε_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 the electric ield (the spherical geometry assumes the value of $A = 1/3$). Eq. (4) predicts the percolation threshold for $v_{2cr} = A$ (for $v_2 \geq v_{2cr}$ phase 2 is partially continuous).

Results and Discussion

Behavior of PC/SAN blends

Temperature dependencies. In Fig. 1a, which shows data for the neat PC in the heating regime, the loss peak (located at T > 165 °C) in the ε''-T plot is clearly seen. This dispersion can be attributed to the primary α-process associated with the cooperative motion of PC chains in the glass transition region[6,7]. The additional α'-process, located at temperatures above the α-process can be attributed to Maxwell-Wagner-Sillars polarization arising at the interfaces between ordered and disordered domains in PC[6]. As expected, its intensity strongly depends on frequency; the temperature position of the peak is 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 is observed in Fig. 1b. This means that the formation of ordered regions requires time which was not sufficient in cooling experiments. For most frequencies at high temperatures, the conductivity contribution in ε''-T dependencies can be seen. The presence of α'-process in the heating run slightly shifts the ε''-T maximum of α-process to higher temperatures (Fig. 1b) and leads to a lower conductivity contribution at high temperatures in comparison with the cooling run.

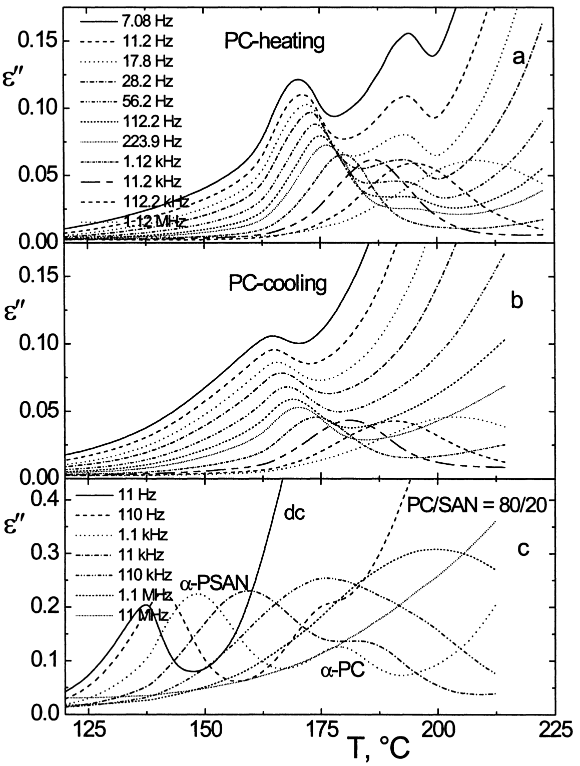

Fig. 1: Temperature dependencies of the loss permittivity ε″ for polycarbonate (a, b) and PC/SAN = 80/20 blend (c) at indicated frequency.

An example of measured temperature dependencies of the loss permittivity ε″ at various frequencies f for PC/SAN blends is shown in Fig. 1c for the 80/20 blend. 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 ≥ 110 kHz, both relaxations overlap and only one broad peak in ε″-T dependence can be seen. Qualitatively similar results were obtained for other PC/SAN blends. Neat SAN shows the simplest dependence of ε″ on T, with only one α-peak and conductivity contribution (ε″ – T curves exhibit a shape similar to the curve shown in Fig. 1c and measured at 11 Hz).

Frequency dependencies. Using the Marquardt procedure for fitting the frequency dependencies, of ε* measured at various temperatures the parameters of Eqs (2) and (3) – the peak frequency f_m, reduced dielectric strength ΔεT, 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 (ΔεT ~ 4000 K) is much higher than that of PC (ΔεT ~ 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 dependencies of the peak frequencies f_m of neat polymers and blends are shown in Fig. 2. In all cases these dependencies obey the WLF equation in the form[1)]

$$\log (f_m/f_s) = -8.86\,(T - T_s)/(101.6 + T - T_s) \qquad (5)$$

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 PC, $\log f_s = 5.6$ (Hz) and $T_s = 201.8$ °C. The temperature dependencies of f_m of both α-relaxations found in blends lie between those of the neat polymers (Fig. 2). The more pronounced shift of α-PC than that of α-SAN with blend composition indicates that larger fraction of SAN is dissolved in PC phase than vice versa[14)] (for 50/50 blend, the PC phase contains ~ 10 wt.% of SAN whereas in SAN phase only ~ 5 wt.% of PC is dissolved).

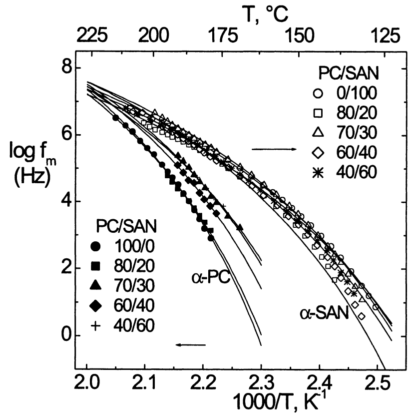

Fig. 2: Temperature dependencies of the peak frequencies f_m of α-processes of individual phases of neat PC and SAN polymers and their blends

In all cases, the shape of α-relaxations was asymmetric; we have found that the HN shape parameters b and c are virtually independent of temperature (for SAN b ~ 0.8 and c ~ 0.5, and for PC b ~ 0.7 and c ~ 0.4). The shape parameters of both α-processes in PC/SAN blends correspond to those of neat polymers. This means that the shape parameters of α-transitions are not sensitive to partial miscibility of components. For all PC/SAN samples, also the conductivity exponent d ~ 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 ΔU ~ 1.3 ± 0.1 eV. Figures 3 a,b show the concentration dependence of storage ε′ and loss ε″ components of permittivity at a low frequency, f = 11.2 Hz, and a high temperature, T = 207 °C (conductivity region). It can be seen that the Böttcher equation (4) with the value of A =1/3 roughly describes the data; this means that the percolation threshold is achieved at $v_{2cr}=1/3$ ($c_{SAN} \sim 0.3$). The effective dipole moments of monomeric unit of SAN and PC, μ_{SAN} and μ_{PC}, calculated from the equation[20,21]

$$\mu^2 = 9\,\varepsilon_0\,k\,T\,(\varepsilon'_0 - \varepsilon''_\infty)(2\varepsilon'_0 + \varepsilon'_\infty)/[N\,\varepsilon'_0\,(\varepsilon'_\infty + 2)^2] \qquad (6)$$

where k is the Boltzmann constant and N is number of monomer units per unit volume, are also plotted as function of the blend composition in Figs. 3c,d.

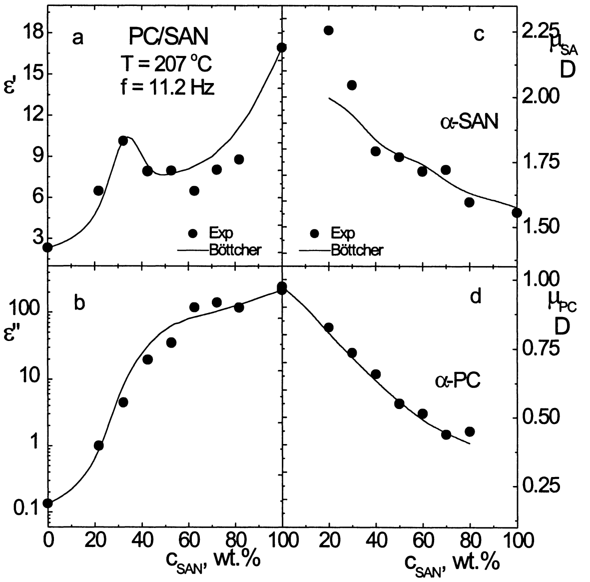

Fig. 3: Concentration dependence of the storage ε′ (a), the loss ε″ (b) permittivity and dipole moments μ_{SAN} (c) and μ_{PC} (d): ● experiment, —— Böttcher equation (4).

The μ_{SAN} value (1.56 D) corresponds well to the theoretically expected (1.80 D) calculated from the SAN composition $(0.24\times3.6^2 + 0.76\times0.5^2)^{1/2}$; also the μ_{PC} value (0.97 D) roughly corresponds to that found for diphenyl carbonate[25)] (0.9 D at 50 °C and 0.7 D at –25 °C). While the increasing concentration of polar SAN component in blend decreases the μ_{PC} value of the PC-rich phase, increasing concentration of less polar PC component in the blend increases the μ_{SAN} value of the SAN-rich phase. The dipole moments dependencies on blend composition can be, at least in the first approximation, described by the Böttcher equation (4) with the value of A = 1/3; this again indicates that the percolation threshold is achieved at $v_{2cr}=1/3$ (c_{SAN}~0.3).

Behavior of PC/PMMA blends

Temperatures dependencies. In accord with the literature,[22-24)] strong overlap of the glass α-transition with the secondary β-relaxation was found for neat PMMA. Two loss peaks corresponding to the α- (T > 120 °C) and β-processes (T < 120 °C) in the ε'' - T plots can be seen only at the lowest frequencies f (up to 110 Hz, Fig. 4a); for higher f strong overlap of α- and β-relaxation takes place and only one broad peak can be observed. Strong dc contribution is detected at the highest temperatures and low f. An example of the measured ε'' - T dependencies for blends is shown in Fig. 4b for PC/PMMA = 60/40 composition. Also in this case, expected three relaxations (α–PC, β-PMMA (T < 120 °C) and α–PMMA (T > 120°C) together with dc conductivity could be detected only for the lowest f.

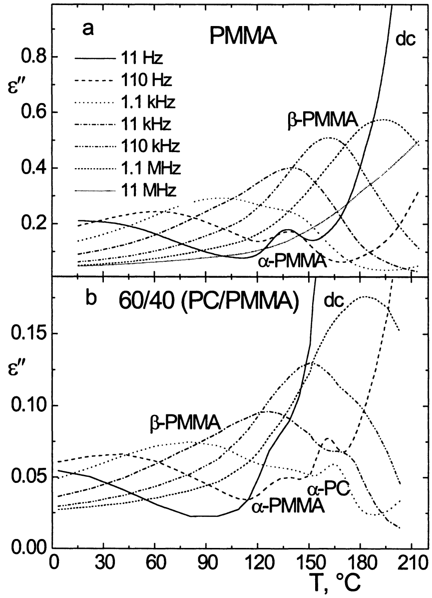

Fig. 4: Temperature dependencies of the loss permittivity ε'' for neat PMMA (a) and PC/PMMA = 60/40 blend (b) at indicated frequencies

Frequency dependencies. The use of the fitting decomposition procedure for PC/PMMA blends allows us to detect only one process for the PMMA phase (αβ-process) in blends. In such a way the parameters of Eqs (2) and (3) could be determined for the α–process PC and for single αβ–process PMMA in blends. Due to the polar carbonyl groups, the reduced dielectric strength of αβ-process PMMA (ΔεT ~ 950 K) is higher than that of PC (ΔεT ~ 175 K) but lower than that of SAN (ΔεT ~ 4000 K). As in PC/SAN blends, both PC/PMMA relaxations are strongly asymmetric with HN b and c parameters virtually independent of temperature and composition (for PMMA, b ~ 0.6; c ~ 0.4 and for PC, b ~ 0.7 and c ~ 0.4).

The temperature dependencies of the peak frequencies f_m of individual relaxations (α-PC and β-PMMA (T < 120 °C) or αβ-PMMA (T > 140 °C)) are shown in Fig. 5 for parent polymers and their blends. For α-PC the f_m-T dependencies obey the WLF equation (5). Expected slight shift of f_m corresponding to the α-PC to lower temperatures (toward the αβ-process of PMMA) can be seen with increasing content of PMMA in blends; a similar shift was observed earlier with increasing content of the SAN component (Fig. 2). As previously, this means that a small fraction of PMMA is dissolved in the PC-rich phase, which confirms partial miscibility of PC/PMMA blends.[24)]

More complex temperature dependencies of f_m can be seen for the relaxations corresponding to the PMMA-rich phase (Fig. 5). From frequency measurements of neat PMMA in the temperature region T ≥ 140 °C, the f_m values of αβ–process could be determined and are plotted in Fig. 5; for T < 140 °C, only f_m values of the αβ-process are plotted. In the first approximation, not only the temperature dependencies of β- but also of αβ-process in the neat PMMA obey the Arrhenius

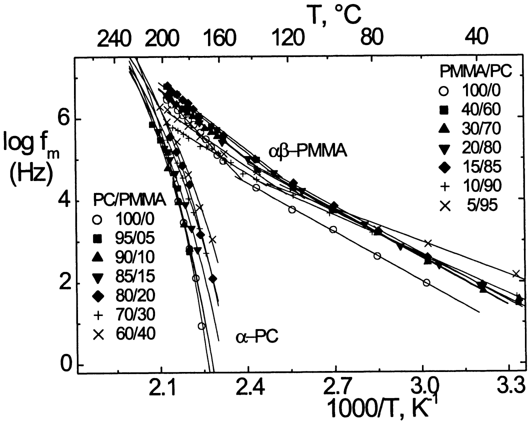

Fig. 5: Temperature dependencies of the peak frequencies f_m for α-process of PC phase and for αβ-process of PMMA phase at indicated concentration.

equation with an average activation energy ΔH = 1.56 eV (at high temperatures) and ΔH = 0.86 eV (at low temperatures). Although for blends only one relaxation process corresponding to the PMMA-rich phase was extracted from the data; the f_m – 1/T dependencies exhibit a change in the slope at T ~ 120–130 °C (Fig. 5). While in the high-temperature region ΔH = 1.13 eV was found virtually independent of the blend composition, in the low-temperature region ΔH increases with increasing PMMA content from 0.5 eV (95/5) to 0.75 eV (60/40). In the high-temperature region, the two highest PC concentrations shift the f_m values of PMMA in the blends to higher T (towards the α-process of PC); such behavior is expected when the components are partly miscible. On the other hand, low PC concentrations in the blends (< 85 wt-%) shift the f_m in the high-temperature region to lower T; we suppose that this unexpected behavior is due to a strong overlap of the α- and β-processes of PMMA in the blends. At lower temperatures (T < 120 °C), the f_m values pass through a maximum in the dependence on PC concentration in the blends. This suggests that both the overlapping effect of αβ-relaxations and the PC content are responsible for the resulting concentration dependence of f_m at T < 120 °C.

The reduced dielectric strength ΔεT of both processes slightly depends on temperature and is proportional to the content of the corresponding blend component (Fig. 6 shows the ΔεT values determined for T = 180 °C). In this figure the effective dipole moments of monomeric unit of PMMA, μ_{PMMA} and PC, μ_{PC} (see Eq. (6)) are also plotted as functions of the blend composition. While the introduction of the polar PMMA component into blends slightly

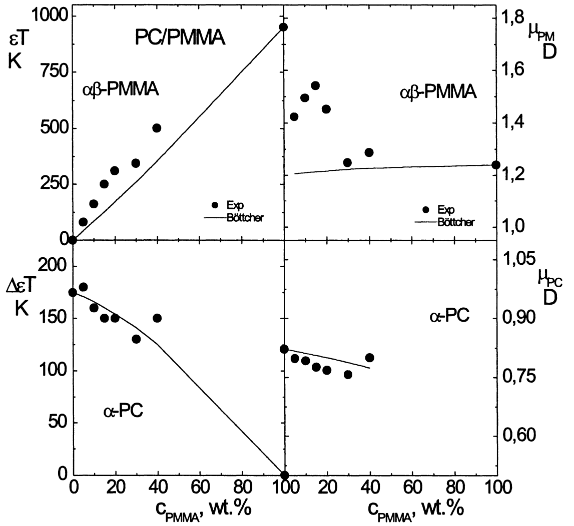

Fig. 6: Concentration dependence of the reduced dielectric strength ΔεT and dipole moments μ_{PMMA} and μ_{PC}: ● experiment, —— Böttcher equation (4).

decreases the μ_{PC} value of the PC-rich phase, the introduction of the less polar PC component into the blend increases the μ_{PMMA} value of the PMMA-rich phase. While the concentration dependencies of $\Delta\varepsilon T$ and μ_{PC} of PC-rich phase roughly correspond to the Böttcher equation (4) with $A = 1/3$ (as in PC/SAN blends), the concentration dependencies $\Delta\varepsilon T$ and μ_{PMMA} values of PMMA-rich phase exhibit pronounced deviations from the Böttcher equation (4). We believe that these deviations are mainly due to overlapping of α- and β-processes in PMMA-rich phase. A more detailed analysis of both relaxations in PMMA-rich phase is in progress.

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