Effect of Low-Molecular Weight Arenes Additives on the Interphase Layer Structure of SAN-PS Systems and Dielectric Behavior of Such Compositions

M. Anoshenko, T. Bazylyuk, N. Iukhymenko, and V. Budzinska

Abstract The influence of low-molecular weight arena's (LMA) on the dielectric behavior of a binary system with limited compatibility between components based on styrene-acrylonitrile (SAN)-polystyrene (PS) copolymers studied. Benzene found to selectively interact with SAN and PS, blocking the polymer–polymer interaction in interphase layer (IPL). The restructuring of the IPL structure in the presence of toluene revealed, as well as the increase in the stabilization of the lyophilic fluctuation network that forms the IPL. Styrene can be used as a compatibilizer of the studied polymer–polymer system. Benzonitrile causes weakening of intermolecular interaction in IPL due to selectivity, as well as dipole–dipole interaction of nitrile groups of the copolymer and benzonitrile. It was concluded that the possibility of the formation of a rigid lyophobic network, as well as the heterogeneity of mixtures of mixtures associated with this process, is controlled, in general, by the content of SAN in the compositions.

1 Introduction

Stable complexes of low-molecular arene-arene systems are known from the literature. These complexes are stabilized by π–π electron conjugation [1–6]. Such an interaction requires a co-planar arrangement of the phenyls of the corresponding components, which in this case is easily achieved.

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On the other hand, the effects of a similar interaction can be expected for systems polymer–polymer with limited compatibility of components. However, in this case, the intermolecular interaction (IMI) process “run into” a significant complication, which is that the phenyls associated with the macromolecule cannot freely to get closer with the corresponding groups of another macromolecule, moreover, cannot show clear coplanarity. In our opinion, there is a possibility of coplanarity correction due to the third component—the low-molecular weight arena (LMWA). In this case, in our opinion, we can expect the formation of a sandwich polymer *A*—LMWA—polymer *B*, if both polymers contain phenyl core in their composition.

Good models for studying the processes of redistribution of IMI forces in the interphase layer (IPL) of polymer–polymer compositions with limited compatibility are systems of copolymer AB-homopolymer B, if component B is non-polar. Compositions whose components are non-polar can form advanced IPL. It is known that mixtures in which a polystyrene component is present can form structures, in which the IPL content is ~ 20%. On the other hand, the interphase layers formed by non-polar polymers are not strong. There is a problem of increasing IMI in these layers. Such are mixtures based on a copolymer of styrene and acrylonitrile and polystyrene (SAN-PS).

On the other hand, the mixtures described above show in the experiment the anomalies of many structurally sensitive characteristics. Such characteristics include, in particular, the dielectric behavior of the corresponding compositions.

The aim of this study was to study the influence of low-molecular weight arenas on the dielectric behavior of a binary system of copolymers of styrene and acrylonitrile-polystyrene.

2 Experimental

The industrial thermoplastic polymers of SAN and PS: SAN of azeotropic composition (the ratio of styrene and acrylonitrile units by gas chromatographic analysis was 62:38) and industrial suspension PS were used in the work.

The viscometric average molecular weight (Mη) was for SAN-54560 (DMF, 20 °C), for PS-237775 (chloroform, 25 °C). The glass transition temperature (T_g) of the SAN was 108 °C, and of the PS was 98 °C (inverse gas chromatography (IGC) method).

Mixing of SAN with PS carried out by extrusion method at temperature 20–30 °C higher than SAN and PS flow temperatures. After the mixing, prepared mixtures were slowly cooled down to the laboratory temperature and crumbled and, for better mixing, re-extrusion performed. The product of double extrusion crumbled again at a liquid nitrogen temperature (to prevent degradation). Samples for the experiment in the form of films prepared by compression at a temperature of 150 °C and a pressure of 100 atm. in fast and slow cooling mode.

As low-molecular weight components benzene, toluene, styrene, benzonitrile (BN) used. LMWA incorporated into a polymer system by sorption of the corresponding liquid under saturated vapor (desiccator method). The amount of LMWA incorporated into polymers was ~ 0.5% wt.% relative to the polymer matrix.

To compare of the relaxation processes in the initial polymers and in the corresponding compositions, the dielectric relaxation method used. The following dielectric parameters, such as the tangent of the dielectric loss angle (tg δ) and dielectric permittivity (ε'), were estimated. Conclusions about the mechanisms of intermolecular interaction changing in the IPL made based on the infrared spectroscopy data (Nexus-475). IR spectroscopic investigations carried out in the range 400–4000 cm^{-1}.

3 Results and Discussion

Analysis of the electrical characteristics in the region of α-relaxation, and especially in the temperature range of crankshaft oscillations (molecular motions of the type "crankshaft"), gives an opportunity to make conclusions about the relative level and redistribution of IMI forces in systems with different ratio of components.

If the manifestation of molecular crankshaft type motions is established in the nature of the PS, then with regarding styrene copolymers (e.g., SAN), such rearrangements can only occur when the copolymers contain styrene oligoads. It was calculated [8] and NMR C13 was used to prove experimentally [9] that SANs (obtained by initiating radical copolymerization at azeotropic ratio of styrene and acrylonitrile) include styrene oligoads, at least dyads and triads. We have analyzed our SAN using IR spectroscopy. The absorption band at 547 cm^{-1} is clearly registered in the spectrum (Fig. 1). According to [9], a copolymer containing styrene (C) sequences of CC and CCC absorb at 550–555 cm^{-1} if the number of styrene sequences is $n =$ 4–5 then at 545 cm^{-1}. Thus, it can be argued that our SAN sample contains styrene dyads, triads, and probably tetrads, and this, in turn, is the basis for the manifestation of molecular motions such as crankshaft oscillations of the crankshaft type.

Figure 2 shows the dependence of tg δ (tangent of dielectric loss angle) on the temperature of the original SAN and the SAN-PS compositions at a frequency of 1 kHz.

We see that in the temperature range 20–60 °C, there is a dipole-group relaxation process, which, in view of [7], we attribute to the manifestation of independent crankshaft oscillations in the styrene oligoads of the SAN and PS.

On the other hand, a study of the basic relaxation process showed that the mixtures are characterized by a single T_α, which, when increasing the PS content, moves to lower temperatures by 3–4 °C. Considering that the glass transition temperatures determined by the inverse gas chromatography method are equal to 108 °C (SAN) and 96 °C (PS), it is possible to state that there is a sufficient level of IMI in IPL of these partially compatible systems, at least in the temperature range 100–140 °C.

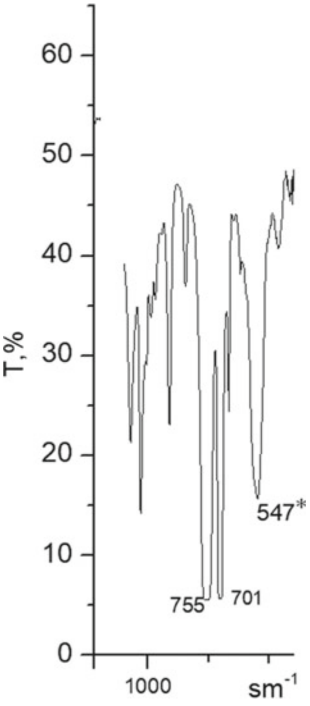


Fig. 1 Fragment of the SAN IR spectrum

Figure 3 shows similar dependencies for SAN-PS mixtures in the presence of LMWA: benzene, toluene, and styrene.

The completely different effect of benzene and its substituted homologues on the polymer–polymer interaction seen.

Thus, in the presence of benzene, active relaxation behavior observed at temperatures in the region of crankshaft oscillations. Therefore, it should concluded that in the temperature range of 35–50 °C, benzene not incorporated into the structure of the polymer–polymer sandwich.

The α-relaxation region in the SAN-benzene system (Fig. 4a) and in the micro-heterogeneous SAN-PS-benzene mixtures (PS content does not exceed 5%) (Fig. 4b) is located at 118–119 °C and this is lower than T_α SAN = 123 °C, which indicates a decrease of IMI in IPL polymer–polymer compositions in the presence of this arenas, and also it indicates that benzene is not played as a plasticizer. The last conclusion supported by the dielectric behavior of a macro heterogenic mixture containing 10% PS Fig. 5.

There is a harsh redistribution of the dipole-segmental losses intensity in behalf of dipole-group losses, and T_α of this mixture is also reduced to 92 °C.

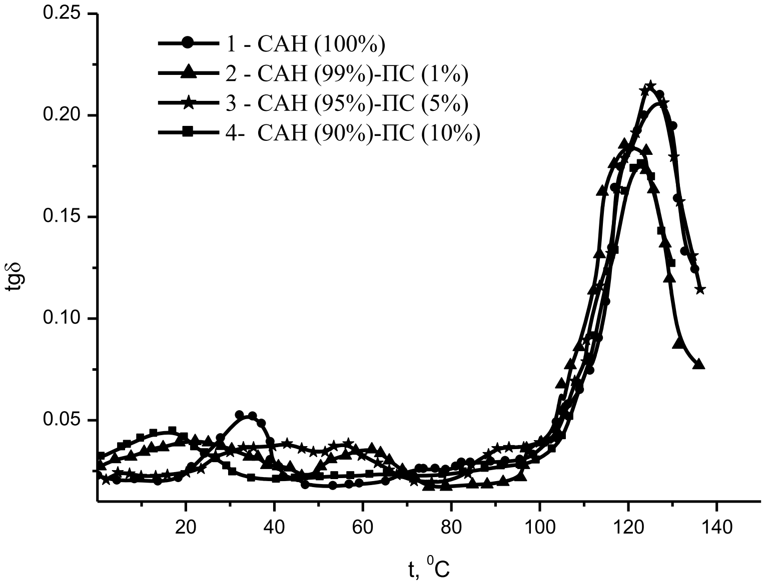
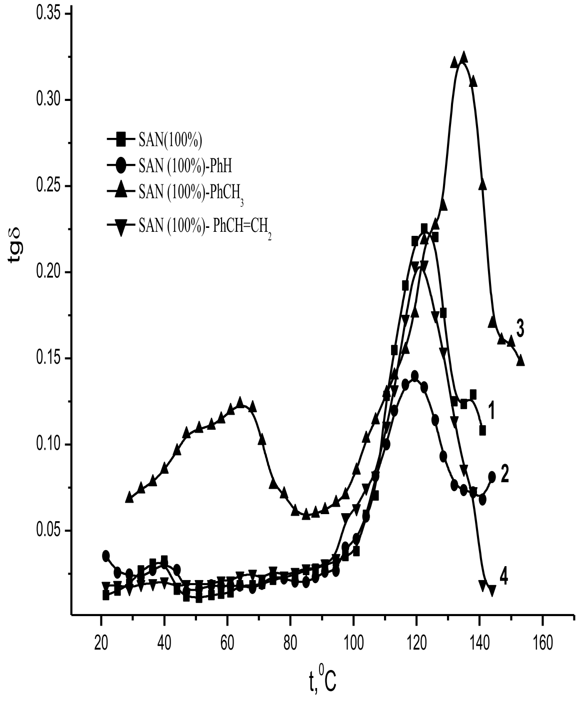


Fig. 2 Temperature dependence of the tangent of dielectric loss angle (tg *δ*) of SAN and SAN-PS compositions

Fig. 3 Temperature dependence of the dielectric loss angle tangent (tg *δ*) of SAN and systems: SAN-benzene, SAN-toluene, SAN-styrene at a frequency of 1 kHz



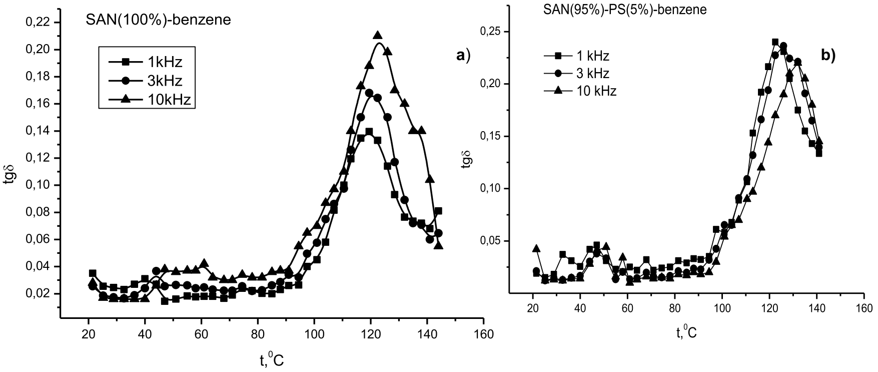


Fig. 4 Temperature dependences of tg δ systems: **a** SAN-benzene and **b** SAN (95)-PS (5%)-benzene at different frequencies

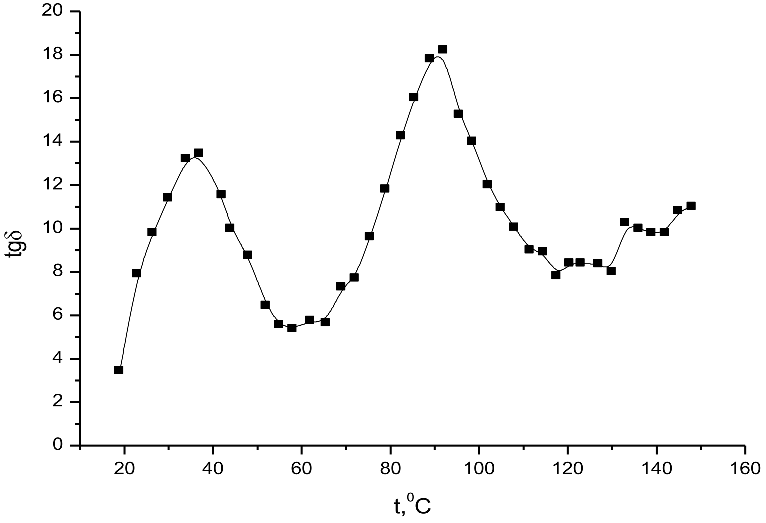


Fig. 5 Temperature dependence of tg δ of the SAN-PS system (10%) at a frequency of 1 kHz

It is known from the literature [9] about the active processes of toluene clustering in the lyophilic matrix of SANs. The dielectric behavior of SAN-toluene and SAN-PS-toluene systems (as part of our experiment) also indicates this possibility: (curve 3, Figs. 3 and 6). Clusters actively formed in the copolymer at temperatures of 40–75 °C, and in a mixture, e.g., SAN: PS = 95: 5-at 60–80 °C. Then, we made conclusion that correlates with the conclusions [9] about structure formation caused by the presence of toluene in the copolymer fluctuation mesh lyophilic component, and probably, in the overall mesh (which also has a lyophilic nature), which is realized in the IPL system SAN-PS. Moreover, the analysis of the temperature position tg $\delta_{\max}$ leads

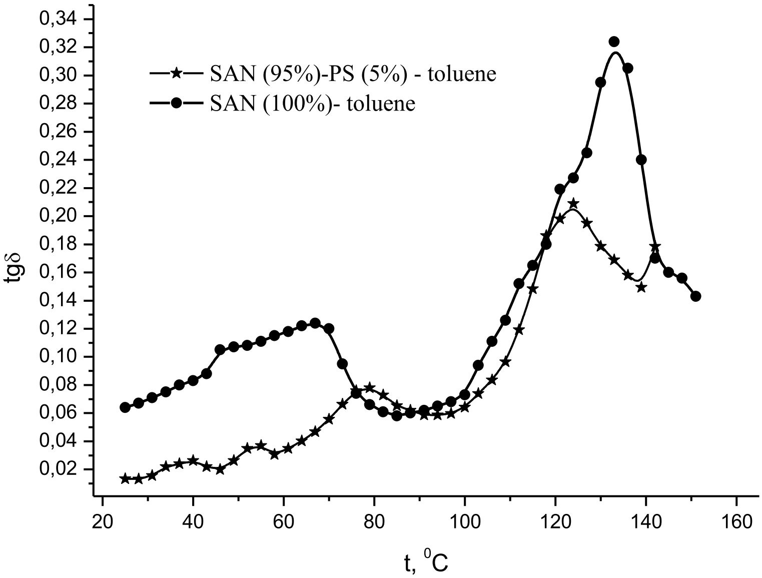


Fig. 6 Temperature dependence of tg δ of the SAN-PS-toluene and SAN-toluene system at 1 kHz

to the conclusion that the IMI in the SAN-toluene-PS system is greater than in the SAN-toluene system.

The presence of styrene (in the amount of ~ 0.5% relative to the polymeric matrix of SAN) completely freezes the dipole-group losses, which are characteristic of molecular motions of the crankshaft type in the SAN and PS. This fact can testify to the formation of overall fluctuation meshes of the lyophilic nature in both the binary SAN-styrene system and the triple SAN-styrene-PS systems. Moreover, the IMI in such meshes is larger than in the matrix copolymer, as evidenced by the temperature position of tg $\delta_{\max}$. This temperature does not drift downwards, even for a macro heterogenic mixture containing 10% PS.

Figure 7 shows that the behavior of SAN-PS-BN mixtures in the range of crankshaft oscillations indicates the selective interaction of phenyls of the corresponding polymers with LMWA; at the same time, the interaction of phenyls of SAN and PS in IPL getting weak. The α-relaxation region for compositions containing benzonitrile changing significantly with any change in the ratio of components in the system. A complex change in the symmetry of the maxima is visible.

The basic maximum tg δ (α-relaxation process) in the binary composition of SAN-BN is observed at ~ 121 °C, and in the triple mixtures of SAN-PS-BN (if PS content does not exceed 5%) at slightly higher (5 and 7 °C) temperatures (Fig. 7). It can be attributed to the fact that in the region of temperatures 100–140 °C increasing the role of rigid lyophobic mesh that compete with lyophilic mesh. Dipole–dipole interaction involving the nitrile groups of SAN and BN is responsible for lyophobic mesh formation.

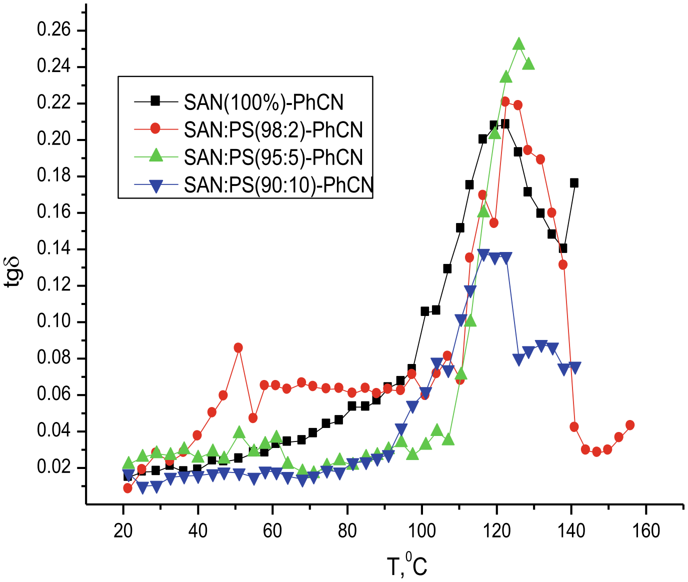


Fig. 7 Temperature dependence of tg *δ* (1 kHz) for composition: SAN-BN-PS

The SAN-PS system (90:10)-BN in the α-relaxation region already shows two maxima tg *δ* (similar to the SAN-PS composition (90:10)-AN), but with a more clear separation effect. The half-width of the peaks increases significantly in the case of this mixture. This indicates a wide distribution of relaxation times and, therefore, of molecular motions responsible for the range of relaxation processes. (Fig. 7.)

It can be said that in the presence of BN, there is a very complex redistribution of IMI forces in the whole spectrum of interphase layers, which is formed by the initial lyophilic mesh of the matrix copolymer and the elements of the lyophobic gmesh formed in the presence of BN. The analysis of temperature and concentration dependences of dielectric constant has not added anything new to our conclusions, so not stated in the paper.

4 Conclusions

Thus, as a study result of the styrene and acrylonitrile copolymer that obtained by the initiated radical copolymerization in mass (azeotropic ratio of the original monomers) by IR spectroscopy proved the presence of styrene dyads, triads and tetrads in SAN macromolecules. Such a structure of macromolecules opens the possibility for the active participation of the styrene component of the copolymer in the redistribution of the IMI forces.

Analysis of the dielectric behavior of the samples showed that under the conditions of our experiment, the corresponding molecular moves (crankshaft oscillations) manifested in the dipole-group loss region (temperature range of 20–60 °C). In addition, the evaluation of the behavior of the polymers studied (in the absence and in the presence of LMWA) in the temperature regions of dipole-group-(crankshaft molecular rearrangements) and dipole-segmental losses showed that in the presence of toluene and styrene the systems behave as the only complexes of SAN-LMWA-PS. This effect manifested despite the different nature of the substituents on the benzene ring: the main thing is that the aromatic compound has an asymmetric distribution of the electron density in the ring. In the first case, the possibility of forming a stable complex is associated with an increase in the electrical charge of the ring of the toluene molecule (compared to the benzene molecule).

The presence of such a strong electron-withdrawing group as vinyl (and the π-double bonds of this group are in conjunction with the phenyl p-electrons) leads to high polarization and delocalization of the electron cloud. Judging by the dielectric behavior of the SAN-styrene-PS mixtures studied by us, this arena may serve as a compatibilizer for them.

Benzene selectively interacts with SAN and PS, blocking interaction in the IPL.

In the case of polymer–polymer, systems containing benzonitrile, the decrease in intermolecular interaction in IPL is obviously associated not only with similar selectivity but also with the possibility of dipole–dipole interaction due to the nitrile groups of the copolymer and benzonitrile. As a result, the complex structure of IPL-s formed by competing (lyophilic and lyophobic) fluctuating meshes. The possibility of forming a rigid lyophobic mesh and the related heterogeneity of the mixtures generally controlled by the content of SAN in the compositions.

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