Nonlinear Loading Effects in Oxide-filled Polyester Nanocomposites Observed by IR-spectroscopy and Lifetime Positron Spectroscopy

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Abstract Impact of nanosized oxide particles of titania (rutile) (TiO_2) and silica-titania fumed compound on physical properties related to inner structure of a styrene-cross-linked polyester resin have been experimentally studied. The IR-spectroscopy and the positron annihilation lifetime spectroscopy (PAL) were used to study the electronic polarizability of interatomic bonds and the positron annihilation processes with increasing the filler loading. All the nanocomposites show unmonotonous variations in the IR-absorption lines and the positron annihilation parameters. Three lifetime components, namely τ_1 , τ_2 , and τ_3 with intensities I_1 , I_2 , and I_3 have been determined. The lifetime loading dependences exhibit non-monotonous lowering within the low loading range ($C_m \leq 5\%$) with the minima values at $C_m \sim 1.5\%$ for the unfilled resin and the nanocomposites. The free-volume portion f_v (in %) in a polymer matrix decreases monotonously for the nanocomposites with STO-particles upon loading while for the TiO_2 -nanocomposites it increases non-monotonously. The parameters describing the supramolecular structure of the nanocomposites have been calculated using the fractal approach. Some correlations between loading-dependent PAL-properties and underlying alterations in the resin's supramolecular structure have been discussed.

Keywords Polyester Resin, Titanium Oxides, Nanocomposite, Positron Annihilation, Positronium, IR Absorption, Fractal Analysis, Supramolecular Structure

1. Introduction

In recent years, nanosized oxides such as SiO_2 [1–6], TiO_2 [7–10], and silica-titania (STO) fumed compound [10] are being intensively employed as fillers to improve electric, mechanic, or thermal properties of various

polymers. Thermosetting polymers with a three-dimensional network structure are more useful in practical applications than thermoplastics because they are harder, more chemically inert and have better mechanical strength and heat resistance due to the high degree of crosslinking between polymeric chains [11]. The unsaturated polyester resin (UPR) used in the present work is a typical example of a good-performing network polymer.

A promising feature of oxide-filled polyester nanocomposites (PNCs) is a possibility of tailoring their parameters by varying filler's loading, particle's size, dielectric permittivity, and number of active surface sites [12–16] because these are the factors which influence on particle-polymer interactions [17]. However, the data related to PNCs show that there is only a little progress in our understanding of particle-macromolecule interaction mechanisms and structure-property relations. Therefore, the question of how to optimize tailoring the physical properties of PNCs for specific/customer needs by varying the above-mentioned filler's parameters still remains one of the most important challenges for applied polymer sciences.

Filling of amorphous glasslike polymers (in particular, UPR) leads to restructuring of polyester and styrene chains, changing a number of unfixed fragments of macromolecule, appearance of double layers with internal electric fields. It has recently been shown that filling the UPR with either titania or silica-titania fumed oxide results in breaking the styrene cross-links and increasing a number of the unlinked moieties [10]. The dependencies of the physical parameters on filler content are characterized by a non-monotonic pattern which is clearly revealed at low filler content. It may be supposed, that the structural adjustment in the polyester nanocomposites is accompanied with electron density distribution among polymer chains, defects, and atomic groups varying their polarizability and dipole moments.

It has early been shown known that epoxy resins [18-23] and other thermosetting polymers [24, 25] can exhibit structural inhomogeneities in nanoscale arising either from decreased miscibility of initial components during a curing reaction or from curing involving other reaction mechanisms. Recent studies which have been made by using the atomic force microscope at fracture interfaces [26-30], IR-spectroscopy [26, 27, 29, 30], and differential scanning microscopy [26, 27] confirmed that epoxy-amine resins possess a heterogeneous, submicrometer nodular structure. Multiple researchers have proposed that these nodular structures are composed of regions of relatively higher cross-linking surrounded by an interstitial phase of relatively lower cross-link density [21, 23, 26, 28]. Therefore, it is reasonable to assume that unsaturated polyester resins, being thermosetting polymers, also possess inhomogeneous, supramolecular structure. Hereafter, we will use the term “cluster structure”, considering tightly packed nodules as clusters and loosely packed nodules as disordered areas. Thus, when speaking about a supramolecular structure of random-particulate polymer nanocomposites one should keep on mind that the structure includes several different locally-arranged areas, namely the nanoparticles themselves, the interfacial regions surrounding the nanoparticles, and the polymeric clusters and disordered areas.

Therefore, it may be suggested that the rearrangement of polyester chains, styrene cross-links, and unlinked atomic groups of polyester and styrene chains within 3D-molecular network induces by nanoparticles will be accompanied by a change in electronic density on atomic, molecular and supramolecular structural scales.

Thus, the present study was undertaken to investigate alterations in the electronic structure of styrene cross-linked unsaturated polyester resin caused by nanosized titanium dioxide and silica-titania fumed oxide with relatively low number of active surface sites. For this purpose, the dynamics of IR absorption and the annihilation of positrons processes induced by filler load changes were monitored. In addition, the parameters describing the supramolecular structure of nanocomposites were evaluated using the fractal method.

2. Materials and Methods

2.1. Materials

A commercially available orthophthalic styrene cross-linked unsaturated polyester resin “Polymal 1094 AWTP-1” (Poland) was used as the UPR matrix. It is a thermosetting polymer of a 3D-network molecular structure [31].

Chemical structure of a typical orthophthalic unsaturated polyester resin can be found elsewhere [32]. It is composed of the polyester macromolecular chains and the styrene

cross-links bridging two polyester chains together. The number of styrene molecules in the link may vary, mainly, from 1 to 3 [33]. Essentially is that not every elementary polyester unit is linked and the unlinked units are randomly distributed along a macromolecular polyester chain.

Titanium dioxide of the rutile form (Ukraine) and the silica-titania fumed oxide (TAS-40, Ukraine) hereinafter referred to as STO, were nanofillers. Oxides differ from each other by the number of active surface sites and the nature of their interaction with resin macromolecules.

The titania particles were characterized with averaged diameter $2R_f \sim 25$ nm and specific surface area $S_f \sim 10$ m²g⁻¹, whereas STO-particles were of $2R_f \sim 40$ nm and of $S_f \sim 40$ m²g⁻¹. For both the fillers their mass loading C_m in the composites varied as 0.5, 1.5, 3.0, and 5.0 %.

The values of S_f were determined by measuring the amount of physically adsorbed nitrogen gas from adsorption-desorption isotherms according to the standard Brunauer, Emmett and Teller (BET) method [34] with Autosorb Station 3 of “Quantachrome Instruments Company” (USA).

The active surface sites (ASSs) of titania surface are TiO (oxygen vacancies with the Ti³⁺ ions) as either Ti→O bonds or O→Ti bonds [3] and TiOH [35]. There are the same centers on the surface of STO, and also SiO, silanol groups Si - OH, siloxane groups Si - O - Si and Ti - O - Si bridges [36]. In general, titania particles contain a small number of active surface areas compared to STO.

Figure 1 compares IR-absorption spectra of silica-titania fumed oxide (the curve “1”), and titanium dioxide (rutile, the curve “2”). One can see that the spectrum of STO (the curve “1”) contains the wide bands of free OH-groups (centered at 3750 cm⁻¹) and of absorption centers of {Ti-O(H)-Ti} (centered at 1454 cm⁻¹). Neither such ASSs nor other ones are not present on the surface of rutile. Thus it is less active catalytically as compared to STO.

Figure 1. IR-reflection spectra of filling nanoparticles –silica-titania fumed oxide (the curve “1”), and titanium dioxide (rutile, the curve “2”)

To remove organic contaminants and adsorbed water

from the surface, the oxide powders underwent thermal treatment at about 400 K during 1.5 hours in air before preparing the nanocomposites.

Nanocomposites were prepared from UPR-solutions mixed by hand with filler in homogeneous mixtures. The polymerization of the mixtures occurred at a room temperature during 72 hours.

2.2. Experimental Methods and Theoretical Tools

Experimental studies were performed using IR-spectroscopy and the positron annihilation lifetime spectroscopy (PALS). The first technique enables to evaluate a deformation polarizability of atomic bonds at atomic level while the second is sensitive at molecular scale (what can be considered as free volume in which positrons are trapped or positronium is formed).

Infrared diffusion reflection spectra were detected at room temperature with the Thermo Nicolet NEXUS FT-IR spectro-photometer in the range of 400-4000 cm^{-1} with the resolution of 2 cm^{-1} .

A fast timing configuration of the “Ortec” positron lifetime system was used to obtain the positron annihilation spectra (see [6] for details). The analysis of the positron annihilation spectra was performed by using the LT-programm [37] with no constraints imposed on the lifetime components.

Finally, some parameters of supramolecular structure have been estimated by using the fractal approach described in [38, 39].

3. Results and Discussion

3.1. The Positron Annihilation Lifetime Spectroscopy

It has been established by using the PAL-technique that three channels of positron annihilation of with intensities I_1 , I_2 , I_3 and the corresponding lifetimes τ_1 , τ_2 , and τ_3 take place in both the unfilled resin and their nanocomposites. The lifetimes correspond to delocalized positrons annihilating directly from defect-free bulk states and from spin singlet para-positronium (τ_1) and to the annihilation of positrons trapped by the structural defects (τ_2), and to the pick-off annihilation of the ortho-positronium atoms captured by extended defects with lowered electron density (τ_3). For the unfilled resin the lifetimes are: $\tau_1 = 204.1$ ps, $\tau_2 = 471$ ps, $\tau_3 = 1914$ ps.

When introducing nanoparticle filler, the lifetimes of the positrons are similar and are characterized by non-monotonic decreases with increasing particle concentration (C_m) reaching the minimum values when the TiO_2 and STO content are equal to 1.5% (see Fig. 2).

Being corrected by a contribution from quasi-free-positron annihilation, $I_1(C_m)$ and $\tau_1(C_m)$ should be replaced by $I_{10}(C_m)$ and $\tau_{10}(C_m)$, respectively [39]

$$I_{10} = I_1 - 4I_3, \quad (1)$$

$$\tau_{10} = \tau_1 + \frac{\tau_1 - \tau_2}{1 + \lambda_0^S \tau_3} \cdot \frac{I_3}{I_{10}}, \quad (2)$$

where $\lambda_0^S = 8 \times 10^9 \text{ s}^{-1}$ is annihilation rate for the para-positronium atom in vacuum. Numerical calculations by using “(1)” and “(2)” show the contribution from quasi-free-positronium annihilation into I_1 is equal 17–19% over the entire loading range and about 3% into τ_1 . Therefore, the loading dependences of both $I_{10}(C_m)$ and $\tau_{10}(C_m)$ remain very close to those of $I_1(C_m)$ and $\tau_1(C_m)$. By other words, the quasi-free-positronium annihilation impact slightly on the annihilation process of free positrons.

Further, taking into account that the annihilation times τ_i are inversely proportional to the related electron densities we may write

$$\tau_1 \sim 1/n_e, \quad \tau_2 \sim 1/\rho_+, \quad \tau_3 \sim 1/\rho_{Ps},$$

where n_e is roughly equal to the average electron density within the polymer chains, and ρ_+ and ρ_{Ps} are electron charge densities on walls of defects trapping positrons and positronium, respectively. Thus, loading dependences of τ_i show variations in electron charge distribution within the annihilation volume of the nanocomposites with increasing the loading. Since the loading dependences of all annihilation times are similar to each other it may be assumed that chain-rearrangement mechanisms underlying increasing n_e , ρ_+ , and ρ_{Ps} for low loadings ($C_m \leq 1.5\%$) are the same.

For both nanocomposites, the dependence of quasi-free positron annihilation (or, in other words, the probability of positron annihilation from a given state) on the doping level is characterized by the occurrence of I_1 minimum that correspond to the maximum of n_e values. This course of dependence I_1 on C_m appears to be related to the reduction of electron density, in areas where annihilation occurs within the first component, for low filler concentrations when $0.5 < C_m < 3\%$.

On the other hand, the growth of electron density (n_e) in polymer chains is accompanied by an increase in both electron density on the walls of positron-trapping defects (ρ_+) and the value of I_2 which is proportional to the probability for positron being captured and annihilate in the trap. Another cause of I_2 growth is increased density of defects (N_+). The correlation between the annihilation parameters I_1 , τ_1 and I_2 , τ_2 indicates what changes in both defect density (N_+) and electron density on defect walls (ρ_{Ps}) result from the restructuring of the polymer chains, in particular, the redistribution of chain's lateral atomic groups which create defect walls.

As for increasing ρ_{Ps} (Fig. 2c), it is also stimulated by the restructuring of polymer chains triggered by nanoparticles.

Figure 2. Loading dependences of annihilation lifetimes: a) τ_1 , b) τ_2 and c) τ_3 for TiO_2 – nanocomposites (the curves “1”) and STO-nanocomposites (the curves “2”)

However, the lack of correlation between the intensity of annihilation of positronium (I_3) and τ_3 indicates that the overall increase of n_e and ρ_+ promotes the diffusion of positronium atoms into regions of lower electron density ($\rho_{ps} < \rho_+$). Such regions are predominantly near the surface of nanoparticles. Distribution of charges and the conformation of chains near a particle’s surface depend essentially on the particle’s density and the number of ASSs on the surface and their chemical activity.

With different activities, ASSs are capable of chemically interacting with unbound polyester chain segments and styrene cross links. In the case of STO particles that have a higher number of ASSs as compared to TiO_2 , the particles interact more intensively with unbound polymer chain segments for $C_m > 1.5\%$ [10], and the ASS chemical bond to the chain segments leads to a reduction in I_3 (capture and annihilation of orto-positronium). It may be due to a reduction in the number of defects trapping positronium (N_{ps}). In the case of TiO_2 particles that have a less active surface, the hydrogen bonding of ASSs with unbound segments dominates, and changes in their conformation

lead to a slight increase of (I_3) and (N_{ps}) at low loadings ($C_m < 1.5\%$) and insignificant declines in both I_3 and N_{ps} at higher loadings (Fig. 3c).

It should be noted that the above-described model of the rearrangement of the polymer structure obtained from the results of annihilation studies is consistent with the model based on data from thermal destruction studies. According to the latter [10], the stabilization process of the polymer structure is realized in polyester resin at low loads of TiO_2 and STO fillers (namely, when $C_m \leq 1.5\%$). Stabilization can be imagine as the healing of three dimensional molecular network imperfections due to the binding of dangling bonds of polyester chains and styrene cross links to ASSs. When the structure of the polymer is stabilized, the number of unbound groups is greatly reduced. As load increases, the polymer structure is destroyed due to an increase in the number of short polyester chains, a number of unlinked polyester segments as well as a number of unbound styrene cross-links.

Figure 3. Loading dependences of intensity of lifetime components: a) I_1 , b) I_2 , and c) I_3 for TiO_2 –nanocomposites (the curves “1”) and STO-nanocomposites (the curves “2”)

According to the model described above, stabilization of

the polymeric structure, occurring for $C_m \leq 1.5\%$, is accompanied by an increase in electron density - density in the polymer chains (n_e) and density on the walls of defects trapping positrons (ρ_+) and positronium atoms (ρ_{Ps}). Increasing n_e is due to decrease of the volume occupied by the chains in nanocomposite, and this process manifests itself as decreasing the intensity of the annihilation I_1 . With respect to the increase of the coefficient ρ_+ , it is most likely to arise from the reduction in the size (R_+) of the corresponding defects. Here, an increase in the intensity of the annihilation I_2 may be due to an increase in the number of N_+ defects. As the load increases above 1.5%, the chain stability is suppressed by their destruction which is reflected in the loading dependencies of inverse parameters (I_1 , τ_1 and I_2 , τ_2).

The radius R_+ can be evaluated from the equation [40]

$$\tau_2 = 0.26 \left[1 - \frac{R_+}{R_+ + \Delta R} + \frac{1}{2\pi} \sin \frac{2\pi R_+}{R_+ + \Delta R} \right]^{-1}, \quad (3)$$

where $\Delta R = 3.823$ is a fitting parameter determined experimentally. In fact, the “(3)” is a well-known Tao-Eldrup equation (see “(4)”) there the factor 0.5 is replaced by 0.26, taking the contribution of positronium annihilation (τ_2) into account. Numerical calculations show that values of R_+ are ranged from 2.92 to 3.44 Å (see Table 1). It can be seen that R_+ loading relationships are not uniform for both nanocomposites and their minimum values fall for $C_m \leq 1.5\%$. This behavior is consistent with the increase of ρ_+ versus C_m for $C_m \leq 1.5\%$.

Annihilation of the positronium atoms and their capture in the well of the potential are described in several models. Tao [41] and Eldrup et al. [42] proposed a model in which ortho-positronium atoms are trapped and annihilated in pores with R_{Ps} radii, which are described as infinitely deep, spherical potential wells of size $R_{Ps} + \Delta R$. The Tao-Eldrup model is adequate only when the pores are less than 1 nm [43] and gives the following relation between the lifetime τ_3 of o-Ps and the pore size R_{Ps} :

$$\lambda_{d,TE}^T(R_P) = \tau_3^{-1} = 0.5 \left[1 - \frac{R_{Ps}}{R_{Ps} + \Delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R_{Ps}}{R_{Ps} + \Delta R} \right) \right], \quad (4)$$

where the factor 1/2 characterizes the spin-state-averaged positronium annihilation rate in the vacuum. The empirical parameter ΔR [40, 42, 44–47] was estimated at 1.656 Å, by adjusting the experimental values τ_3 obtained for material with well-known pore sizes. However, this parameter is the same for all materials and is interpreted as the thickness of the electronic layer located on the wall of the potential well, where the positronium and core electron wave functions overlap.

The volume portion of positronium-trapping pores in a polymer matrix or, by other words, the free-volume portion f_V (in %) can be estimated from the values of I_3 (in %) and

R_{Ps} (in Å) using the relation [40, 42, 44–47]:

$$f_V = 0.0018 \times I_3 \times \left(\frac{4}{3} \pi R_{Ps}^3 \right) \quad (5)$$

As an alternative to the Tao-Eldrup model, Ito and coworkers proposed a semi-phenomenological model describing an ortho-positronium annihilation process developed in large spherical cavities. Within this model, although the pore appears again as an infinitely deep well of potential in which the ortho-positronium atom trapped by the wall is no longer represented by the wave function of the standing wave, it behaves more like a quantum particle bouncing back and forth between the barriers energy wells. This ortho-positronium behavior describes a Gaussian wave package and assumes its annihilation in two mechanisms - 1) as an internal annihilation process 3γ , which occurs in the central pore region of $R_{Ps} < R_A$; and 2) as the pick-off annihilation process due to interaction with a core electron within the pore wall that takes place near pore walls for $R_{Ps} \geq R_A$. In other words, when calculating the ortho-positronium annihilation rate in large pores (λ_d^T) the value of λ_V^T cannot be neglected.

Table 1. Loading dependences for positron- and positronium-trapping defect radii (R_+ and R_{Ps})

Samples	C_m (%)	R_+ (Å)	R_{Ps} (Å)
The resin (UPR)	0.0	3.44	2.77
TiO ₂ nanocomposites	0.5	3.18	2.75
	1.5	2.94	2.74
	3.0	3.28	2.78
	5.0	3.26	2.77
STO nanocomposites	0.5	3.17	2.76
	1.5	2.92	2.74
	3.0	3.01	2.76
	5.0	3.27	2.79

Therefore, the following simple relation was deduced in [48] for estimating λ_d^T :

$$\lambda_{d,Ito}^T(R_{Ps}) = \begin{cases} \lambda_{d,TE}^T(R_{Ps}) + \lambda_V^T, & (R_{Ps} < R_A) \\ \lambda_{d,TE}^T(R_A) + \left[1 - \left(\frac{R_{Ps} - R_A}{R_{Ps} + R_A} \right)^b \right] + \lambda_V^T, & (R_{Ps} \geq R_A) \end{cases} \quad (6)$$

Here R_A and b are the empirical parameters equal to: $R_A = 0.8000$ nm, and $b = 0.55$, $\lambda_V^T = 1/142$ ns⁻¹ (ortho-positronium annihilation rate in vacuum). The parameter $R_A + \Delta R$ characterizes the size of a Gaussian wave package or the effective radius of an ortho-positronium atom in a pore. It is seen from “(3)” that $\lambda_{d,Ito}^T \rightarrow \lambda_V^T$ when the pore size increases infinitely ($R_{Ps} \rightarrow \infty$).

Gidley and co-authors have proposed another model of interaction between ortho-positronium and polymer material, in order to estimate the pore size of several nanometers [48, 49]. Here again it is assumed that the potential well describing the pores is infinitely deep in energy, but has a rectangular shape of L_1 , L_2 , L_3 along the X, Y and Z axes respectively. Thus, the pore size are $L_1 - \Delta R$, $L_2 - \Delta R$, and $L_3 - \Delta R$. The use of rectangular geometry instead of spherical in model wells avoids troublesome calculations based on Bessel functions. The following relationship was obtained for the $\lambda_{d,G}^T$ parameter:

$$\lambda_{d,G}^T = 1/\tau_3 = 0.5 \left\{ 1 - \prod_{n=1}^3 \left[1 - \frac{2\Delta R}{L_n + 2\Delta R} + \frac{1}{\pi} \sin \left(\frac{2\pi \Delta R}{L_n + 2\Delta R} \right) \right] \right\} \quad (7)$$

Table 2 presents the experimental values of lifetime τ_3 and related intensity I_3 for unfilled resin and its nanocomposites. (Here, the standard deviation values are shown as $\pm$ additions).

Figure 4 shows loading dependences of the normalized free-volume portions, i.e. $f_v(C_v)/f_v(0)$, calculated for the polyester resin nanocomposites filled with TiO_2 (Fig. 4a) and STO (Fig. 4b) using models of Tao-Eldrup (1), Ito (2), and Gidley (3). Here C_v is the volume loading. According

to these models, positronium-trapping defect radius for the unfilled resin equals to 2.77 Å, 2.82 Å, and 5.53 Å, respectively. According to the Tao-Eldrup model, the free-volume portion of unfilled resin equals to 2.17 %.

The values of R_{ps} calculated by using “(4)” are given in Table 1. It can be seen that R_{ps} changes with C_m increase are small compared to those obtained for R_+ . Indeed, the relative reduction of the R_{ps} , i.e. $\Delta R_{ps}/R_+(0)$ is 14–15% whereas $\Delta R_{ps}/R_{ps}(0)$ is about 1.1%. Such a discrepancy between $R_{ps}(C_m)$ and $R_+(C_m)$ proves that the positron- and positronium-trapping defects are of different nature.

Table 2. Lifetime τ_3 and related intensity I_3 for unfilled resin and its nanocomposites

Samples	C_m (%)	I_3 (%)	τ_3 (ps)
The resin (UPR)	0.0	13.56 (± 0.32)	1914.0 (± 15)
TiO₂ nanocomposites	0.5	14.00 (± 0.27)	1896.7 (± 5.8)
	1.5	13.98 (± 0.36)	1887.0 (± 11)
	3.0	13.50 (± 0.35)	1925.0 (± 10)
	5.0	13.59 (± 0.30)	1912.0 (± 14)
STO nanocomposites	0.5	13.49 (± 0.36)	1904.0 (± 13)
	1.5	13.52 (0.35)	1886.0 (7.9)
	3.0	12.68 (± 0.35)	1908.0 (± 14)
	5.0	12.45 (± 0.32)	1944.0 (± 12)

Figure 4. Loading dependences of the normalized free-volume portions calculated for the polyester resin nanocomposites filled with: a) TiO_2 and b) STO using Tao-Eldrup (black squares), Ito (red circles) and Gidley (blue triangles) models

In addition, there is no correlation between $I_3(C_m)$ and $R_+(C_m)$. I_3 is proportional to the number of positronium-trapping defects per unit volume (N_{Ps}) and the latter is related to R_{Ps} by the equation [50]

$$\nu_{Ps} = 4\pi D_{Ps} R_{Ps} N_{Ps}, \quad (8)$$

where ν_{Ps} is positronium trapping rate and D_{Ps} is positronium diffusion coefficient. Since for polymers, D_{Ps} is constant and equals to about $10^{-8} \text{ m}^2 \text{ s}^{-1}$ [51, 52], the absence of correlation may be due to the fact that ν_{Ps} varies with increasing C_m . The relation [53]

$$\nu_{Ps} = \left(\lambda_f - \tau_2^{-1} \right) (4I_3 / 3I_{10}), \quad (9)$$

where λ_f is quasi-free positron annihilation rate, suggests that a discrepancy between $I_3(C_m)$ and $\nu_{Ps}(C_m)$ is due to dependences of both I_{10} and $1/\tau_2$ versus C_m . The value $1/\tau_2$ is attributed to the contribution of positronium annihilation occurring within positron-trapping defects. Developing that channel of annihilation seems quite likely due to relatively large radius of positron-trapping defects compared to those of positronium – trapping ones, namely $R_+ > R_{Ps}$.

The models show that both the pure resin and its oxide nanocomposites contain an effective free volume of subnanometer size. It means that the actual size of these volumes is indeed so small that the effect of ortho-positron self-annihilation can be neglected.

As it is seen in Fig. 4, the three models give the identical loading dependences of $f_V(C_V)/f_V(0)$ for nanocomposites. However, $f_V(C_V)$ – dependences for TiO_2 – and STO – nanocomposites are different from each other. For the TiO_2 – nanocomposites f_V increases slightly for $C_V \leq 0.002$ ($C_m \leq 0.5\%$) and then f_V decreases slowly and non-monotonously when C_V increases further. For the STO – nanocomposites, f_V decreases gradually with increasing C_V . The absolute values of the f_V parameter in Tao-Eldrup and Ito models are very close to each other, but in the Gidley model they are higher because of a greater size of pores.

Variations in the free-volume may be due to changes in the number of styrene molecules in the cross-links and the redistribution of positronium-trapping defects due to distortions in the 3D-network molecular structure induced by inner mechanical tensions in the polymer structure. The latter have earlier been revealed by measuring the mechanical parameters of composites [10].

Thus, the nature of the defects that capture the positron and positronium is different. The first are located in a bulk of the 3D-molecular network and the walls of the defects are formed by moieties of polyester chains and styrene cross-links. The second ones are localized near surface of the filling nanoparticles, where walls of the defects are formed by the moieties connected with active surface sites. The molecular conformation of the walls depends on a type of the chemical bonds formed. Positron-trapping defects

are located in regions of a greater electron density ρ_+ and they are larger in size than the size of positronium- trapping defects because $R_+ > R_{Ps}$. Positronium atoms annihilate mainly in the regions located near particle's surface where the electron density is smaller namely $\rho_{Ps} < \rho_+$.

3.2. The Supramolecular Structure of the Neat Resin and Its Nanocomposites

3.2.1. Calculation of the supramolecular structure parameters

Besides unavoidable nanosized pores, the supramolecular structure of the polymer matrix may also influence the positron-matrix interaction and result in some features of loading dependences of positron annihilation parameters. In the polyester resin and its random-particulate nanocomposites the units of the supramolecular structure are ordered regions of 3D-network molecular structure (so-called clusters), disordered regions surrounding clusters, and interphase areas surrounding nanoparticles [38, 39]. It's essentially that all the supramolecular units are the fractal objects [39, 54, 55].

To predict possible impact of the supramolecular structure on features of the positron annihilation, the fractal approach developed elsewhere [38, 39, 56, 57] have been used to evaluate supramolecular structure parameters, namely relative portions of clusters (ϕ_{CL}), disordered areas (ϕ_{DA}), and interphase areas (ϕ_{IPR}). The fractal approach enables the calculation of the special fractal dimensions of the fractal objects by measuring the relationships of the mechanical modules that combine these dimensions with the parameters of the supramolecular structure, molecular characteristics of a host polymer matrix, and geometrical parameters of the filler.

The volume portion (ϕ_{DA}) of the disordered (loosely-packed) regions in a nanocomposite can be evaluated as:

$$C_V + \phi_{IPR}(C_V) + \phi_{CL}(C_V) + \phi_{DA}(C_V) = 1, \quad (10)$$

where ϕ_{CL} is the volume portion of clusters which is the measure of a local order in a polymer [58], ϕ_{IPR} is the volume portion of the interphase regions surrounding the nanoparticles. The values of ϕ_{IPR} and ϕ_{CL} have been evaluated by using the calculation procedures presented in [59] and [53], respectively.

For these procedures, the most essential parameters are the fractal dimension of nanoparticle's surface (d_n) [60] and the fractal dimension (d_f) of solid-state polymers and its nanocomposites [61]. d_n have been calculated through the particle's radius R_f and specific surface area S_f of the particles using the formula [59]:

$$d_n = 3 + \frac{\ln\left(\frac{S_f}{420}\right)}{\ln(R_f)} \quad (11)$$

d_f have been calculated using the following relation [62]:

$$d_f = 2(1 + \nu), \quad (12)$$

where ν is the Poisson's ratio. The dependences of ν versus C_m for the polyester resin nanocomposites filled with TiO_2 or STO were obtained from the ultrasonic measurements [10].

Calculations show that supramolecular structure of the UPR with oxide nanoparticles undergoes some variations. Figure 5 shows the loading dependences of the normalized cluster structure parameter, namely $\varphi_{DA}(C_V)/\varphi_{DA}(0)$. For the unfilled resin $\varphi_{CL} = \varphi_{CL}(0) = 35.5\%$, $\varphi_{DA} = \varphi_{DA}(0) = 64.5\%$. Since the values of φ_{IPR} and $C_V(C_m)$ grow droningly with increasing C_m for both the nanocomposites, it's obvious from "(10)" that the dependences of φ_{CL} versus C_V are always opposite to those of φ_{DA} .

For the TiO_2 -nanocomposites, the cluster structure destructs droningly with increasing C_V , since φ_{DA} increases to 76.1% at $C_V = 1.5\%$. For the STO-nanocomposites, the cluster structure varies differently with increasing C_V . At first, φ_{DA} decreases at $C_V \leq 0.56\%$ to $\varphi_{DA}(0.56\%) = 58.2\%$, then it increases to 64.2% at $C_V = 1.13\%$, and it decreases again to 61.7% at $C_V = 1.9\%$.

Figure 5. Loading dependences of the normalized portion of disordered areas in the UPR nanocomposites filled with TiO_2 (the curve "1") and STO (the curve "2")

3.2.2. Particle-trapping defects and the supra-molecular structure

Clusters, disordered areas, and nanoparticles themselves are nanocomposite's structural units where ortho-positronium atoms can penetrate to and annihilate inside. When comparing loading dependences of the fractal parameters (see Fig. 5) and positron-annihilation parameters (see Fig. 4) one can see a correlation between

$\varphi_{DA}(C_V)$ and $f_V(C_V)$ for both nanocomposites. Namely, for TiO_2 -nanocomposites, non-monotonous increasing of f_V for $C_V \leq 0.14\%$ followed by decreasing it for $C_V > 0.14\%$ meets the similar behavior of φ_{DA} . In STO-nanocomposites, a qualitative correlation between $\varphi_{DA}(C_V)$ and $f_V(C_V)$ is observed – these parameters decrease as the value C_V increases. Correlation indicates that the ortho-positronium atoms diffuse into disordered areas of the supramolecular structure and they annihilate inside. It can therefore be concluded that for both nanocomposites positronium atoms annihilate mainly within the disordered areas of the 3D-polymer network structure.

3.3. The IR-absorption Data

IR-absorption spectra for the unfilled resin and its nanocomposites filled with 0.5, 1.5, 3.0, and 5.0% TiO_2 and STO are shown in Fig. 6. It's remarkable that the resin filling with either TiO_2 - or STO-nanoparticles does not cause disappearance lines or appearance of new ones. On the other hand, by analyzing the spectra closely, it can be seen that the resin absorption lines exhibit slight frequency shifts after filling it with nanoparticles.

Figure 6 shows that the principal effect of resin-doping by nanoparticles, visible in IR spectra, is the non-monotonic relationship of line intensity for both nanocomposites, which is observed with increasing filler loading in the range of $0 \leq C_m \leq 3.0\%$. In general, the effects of load on IR line intensities indicates the variability in electronic polarization of interatomic bonds [63] as a result of both dipole moment changes and redistribution of electron density accompanying the change in polymer structure in both nanocomposites.

There is a correlation between n_e and intensities $I_i(\omega)$ of the lines associated with absorption by dipole groups localized in both polyester chains and styrene cross-links. For example, $-\text{C}=\text{O}$ moieties located in the polyester chains are distinguished by a strong absorption peak at 1738 cm^{-1} related to their stretching vibration. Two absorption lines located at $\sim 1870 \text{ cm}^{-1}$ and 1945 cm^{-1} correspond to the overtones of stretching vibration of the $\text{C}=\text{C}$ bonds in the styrene molecules while the wide absorption band in the range of $3012\text{--}2785 \text{ cm}^{-1}$ with minimum at $\sim 2951 \text{ cm}^{-1}$ is due to superposition of vibrations of $-\text{CH}$ -moieties built in the polyester chains and $-\text{OH}$ -groups bounded with the hydrogen bonds.

Loading dependences $I_i(C_m)$ for dipole moieties located both in polyester chains and styrene cross-links are similar.

Figure 6. The IR-absorption spectra for the unfilled resin (the curves “1”) and its nanocomposites (the curves “2”-“5”) filled with: a) TiO_2 and b) STO at different filler loadings: 0.5% (the curves “2”), 1.5% (the curves “3”), 3.0% (the curves “4”), and 5.0% (the curves “5”)

Dependencies show their non-monotonic increase in the range of $0 \leq C_m \leq 1.5\%$ with a maximum at $C_m = 0.5\%$ for TiO_2 -nanocomposites and increasing in the range of $0 \leq C_m \leq 3.0\%$ with a maximum at $C_m = 1.5\%$ for STO -nanocomposites. In TiO_2 -nanocomposites increase intensity when $C_m \leq 1.5\%$ coincides with rising n_e , but the intensity $I_i(\omega)$ falls in the region of $1.5\% \leq C_m \leq 3.0\%$ where n_e grows further. In STO -nanocomposites, the loading regions in which both $I_i(\omega)$ and n_e grow are compatible.

Each i -th intensity $I_i(\omega)$ is proportional to the number of N_i of absorbing dipole moieties of the i -th type being in an unexcited state and occupying the sample's volume V , and to the squared matrix element $|\langle \mu_i \rangle|^2$ of molecular dipole moment μ_i , according to the expression [64]:

$$I_i(\omega) \propto \frac{N_i |\langle \mu_i \rangle|^2}{3\epsilon_0 \hbar V} A(\omega_i - \omega), \quad (13)$$

where ϵ_0 is the dielectric constant, $\hbar$ is the Planck constant, ω_i is the frequency of the IR transition, $A(\omega_i - \omega)$ is the relaxation parameter characterizing the line width. A quantum-mechanical calculation yields the following expression [65] for the mean dynamic molecular polarizability of the i -th dipole moiety (α_i) via μ_i :

$$\alpha_i(\omega) = \frac{2}{3\hbar} \sum_{n \neq 0} \frac{\omega_{i,n0} |\langle \mu_i \rangle|^2}{\omega_{i,n0}^2 - \omega^2}, \quad (14)$$

where $|\langle \mu_{i,n0} \rangle|^2 = \langle \mu_{i,n0} \rangle \langle \mu_{i,n0} \rangle^*$ and $\hbar \omega_{i,n0} = E_{i,n}^{(0)} - E_{i,0}^{(0)}$. (Here, the subscript “(0)” indicates the ground state of the moiety, the subscript “n” indicates their n -th excited state, and the superscript “0” indicates that the energy is evaluated in absence of incident IR-electric field.) Note, that frequency ω_i measured experimentally should be treated so as to be so close to one of the electronic transition frequencies ($\omega_{i,n0}$) of the moiety that its contribution dominates the frequency dependence of I_i as a

whole. Taking “(14)” into account, “(13)” can be rewritten as:

$$I_i(\omega) \propto \frac{N_i \alpha_i(\omega)}{\epsilon_0 V}. \quad (15)$$

Thus, the intensity of the i -th line is proportional to the volume density of dipoles (N_i/V) and to their polarizability α_i . According to “(14)”, the polarizability α_i depends on the characteristic frequencies $\omega_{i,n0}$ which are determined by an interaction of the i -th dipole moiety with its neighboring molecular environment. It is the interaction that is represented quantitatively by a set of energy values $\{E_{i,n}\}$.

When the polymer is filled with nanoparticles, a conformation of molecular environment for the every i -th dipole varies due to binding or bonding chain fragments to ASSs. As a consequence, both the polarizability α_i and the related intensity I_i vary too. It's remarkable that a nature of chemical binding between polymer chains and ASSs has a significant impact on the chain conformations for both nanocomposites. Different surface reactivity of oxides and chemical bonds lead to different conformations of the polymer chains near the filling particles in TiO_2 - and STO -nanocomposites. This is due to the discrepancy between dependencies of $I_3(C_m)$, especially when $C_m \geq 1.5\%$ (see Fig. 2c). Therefore it can be assumed that for TiO_2 -nanocomposites decreasing of intensity I_i comes from decreasing α_i for moieties surrounding particles.

With filler growth, namely when $C_m \geq 3.0\%$, the intensity of the absorption lines increases moderately for TiO_2 -nanocomposites and slightly for STO -nanocomposites. Under such loadings two processes take place simultaneously, namely, breaking the styrene cross-links and fastening unlinked fragments to ASSs. Both processes have the opposite effect on the polarizability of IR-active dipole moieties, therefore, their absorption intensity versus load is determined by their total effect on the dipole in the composite volume.

3.4. TiO₂ – STO Controversy

It may be suggested that there two main reasons for different behavior of TiO₂ and STO embedded into UPR. The first reason is appearance of so-called interphase regions (IPRs) which surround the nanoparticles embedded in a polymer matrix as a result of peculiarities of particle-resin interaction due to differences in both number and status of ASSs. Analyzing generally accepted chemical structure of the resin and nature of particle's ASSs, one can see that the interaction between macromolecular chains and embedded oxide particles occurs mainly via hydrogen bonding between the surface hydroxyl groups (–OH) of the particles and either the oxygen (–O–) and methyl groups (CH₃) in the backbone of polyester chains or methyl groups terminated the free styrene cross-links (see, for example, the details in [66]). Forming IPRs in random-particulate polymer nanocomposites have earlier been shown by various experimental studies [7, 67–69] and theoretical calculations [70–73] and several phenomenological models have been proposed to give qualitative description for the molecular structure of an individual IPR [74–76]. For example, in nanocomposites of polydimethylsiloxane filled with titania nanoparticles (of 20–40 nm in diameter) formation of IPRs have been suggested to result from strong hydrogen bonding between polymer chains and hydroxyl groups present on the surface of nanoparticle and the thickness of the regions was estimated to 3–5 nm [69].

The second reason is a formation of the electric double layer due to a difference in the dielectric permittivity between filler and a polymer [77]. Indeed, the intrinsic dielectric permittivity of the 13-nm-sized TiO₂-particles makes about 60 within the frequency range of 10³–10⁵ Hz [78] exceeds the permittivity of the neat resin which is about 4.5 at 10 kHz [79] whereas the permittivity of STO is close to the latter [80]. It can be suggested that short polar moieties such as unlinked fragment of polyester chains or individual styrene cross-links will contribute into DELs in UPR-based particulate nanocomposites. Details on physical nature of the DEL itself are available in textbooks on electrochemistry [81, 82] and in many physical chemistry texts [83, 84].

Further details concerning for different behavior of TiO₂ and STO nanoparticles in the polyester resin have been extracted from studying mechanical properties, a thermal desorption process can be found elsewhere [85].

3.5. Remarks on Structure-Property Relations of the Nanocomposites

As it was noticed in the Introduction, polyester resins as well as epoxy-amine resins derive their physical properties from their complicated, highly cross-linked molecular 3D-network having inhomogeneous (so-called nodular or clusterous) supramolecular architecture at nano-scale, which contains domains with different levels of cross-linking. It's generally accepted, as a result of multiple researches, that thermoset's supramolecular structures are composed of areas of relatively higher

cross-linking (or clusters) surrounded by an interstitial phase of relatively lower cross-linking (or disordered areas) [26, 27, 29–31]. These inhomogeneous 3D-network molecular structures drive important physical performance characteristics of thermosets such as modulus, thermal response, solvent/water ingress, and fracture behavior [26, 27 and references herein]. Just as differences in bulk crosslink density and free volume portion lead to different bulk physical and chemical properties, it is reasonable to expect that localized differences in crosslink density, mechanical density, and charge density will lead to local regions with different properties. However, as we know from the literature, no quantitative estimates on supramolecular structure-property relations on random-particulate polyester nanocomposites have been obtained till now. Therefore, we make first careful steps to unveil the issue. An impact of both TiO₂ and STO nanoparticles on mechanical, thermal stability and dielectric properties of the unsaturated polyester resin has been experimentally studied by in our recent publication [85, 86].

Structural alteration occurring in the nanocomposites at mesoscale, when spatial dimensions of pores capturing positrons and positronium are comparable with size of clusters, can be unveiled analyzing dependences of nanocomposite's dielectric permittivity (ϵ_1) versus either volume portion of cluster (ϕ_{CL}) or volume portion of disordered areas (ϕ_{DA}). Combining correspondent experimental loading dependences of ϵ_1 [86] with calculated loading dependences of ϕ_{CL} we've replotted loading dependences of dielectric permittivity of both TiO₂- and STO-nanocomposites into their dependences versus ϕ_{CL} and ϕ_{DA} on Figs. 7a and 7b, respectively.

Here, it should keep on mind that STO-particle occupies an intermedium position (in its values of specific surface area and dielectric permittivity) between titanium dioxide (rutile) and fumed silica, since S_f increases and ϵ_1 decreases when moving from TiO₂- to SiO₂-particles. When comparing the two plots presented on Fig. 7a, one can see three peculiarities occurring in the dielectric reply of a nanocomposite due to that TiO₂-filler is replaced by STO- one. The first peculiarity is enhancing the reply and its non-monotonicity at low loadings, when $0.28 \leq \phi_{CL} \leq 0.36$. In contrast, the non-monotonicity in $\epsilon_1(\phi_{CL})$ for TiO₂-nanocomposites, which is visible at $0.36 \leq \phi_{CL} \leq 0.38$, is relatively weak. The second peculiarity is in shifting the reply towards a region of low cluster content. By other words, such a behavior of $\epsilon_1(\phi_{CL})$ -plot reveals that STO-nanoparticles trigger more considerable structural alterations in the resin. These alterations are characterized by disordering 3D-network structure due to disruption of styrene cross-links and to binding polar moieties of the resin's chains to ASSs. It may be suggested that cluster-size distribution takes place and clusters are randomly distributed over resin's bulk varies with increasing loading. Finally, the third peculiarity is lowering a spread of ϵ_1 -values.

Figure 7. Dielectric permittivity of TiO₂- (the curves “1”) and STO - nanocomposites (the curves “2”) versus: a) relative volume portions of clusters - φ_{CL} and b) disordered areas - φ_{DA}

A similar behavior is demonstrated by ϵ_1 with increasing volume portion of disordered areas (φ_{DA}), as shown in Fig. 7b. The $\epsilon_1(\varphi_{DA})$ -plot for STO-nanocomposites is shifted towards higher values of φ_{DA} and non-monotonous variations in ϵ_1 are enhanced at low loadings. An essential consequence resulted from the non-monotonicity is that ϵ_1 -values measured at different loadings (C_m) are proved to be equal. Then, taking into account that both positrons and positronium atoms annihilate mainly within the disordered areas of the nanocomposites, one can conclude that energy of their coulomb interaction with molecular environment ($e^2/\epsilon_1 r$) would be the same at different loadings. By other words, at low filler loadings disordered islands may arise in the vicinity of STO-nanoparticles and the annihilation processes within the islands will differ from those within disordered areas remotest from the particles. Both the sources contribute into parameters I_2 , I_3 , τ_2 , and τ_3 and determine peculiarities of their dependencies on the loading (C_m).

4. Conclusions

1. The unmonotonic character of the load dependencies of the positron annihilation parameters, such as lifetimes, their intensities, and the free volume portion are related to (i) redistribution of bonded electric charge along both the polyester chains and the styrene cross-links and (ii) rearrangement in spatial configuration of nanosized defects trapping positrons and positronium atoms. Both the effects may be treated as a result of alterations occurring in a 3D-network molecular structure of the resin.

2. Radii of the defects have been calculated by using various theoretical models of positron annihilation. Calculations show there is no correlation between the probability for positrons to be trapped and a number of the defects.

3. For the TiO₂-nanocomposites, the free volume portion

varies slightly with increasing load, while in the case of the STO-nanocomposites it decreases essentially. The latter effect is likely to result from decreasing a number of styrene molecules making up the cross-links due to higher chemical activity of STO-surface as compared to TiO₂-nanoparticles.

4. Regardless of the filler, the loading dependencies for the IR absorption peak intensities are not monotonic for both bending and stretch vibrations of the moieties constituting either the polyester chains or styrene cross-links.

5. The loading effects observed in both the absorption line intensity and positron annihilation parameters indicate that both fillers have a stabilizing effect on the molecular structure of polymer for low loadings (i.e., when $C_V \leq 0.0014$ for TiO₂- or $C_V \leq 0.0056$ for STO-nanocomposites). An underlying mechanism for the stabilizing effect is decreasing a number of unlinked chain's fragments.

6. Fractal analysis shows that filling the polyester resin with oxide nanoparticles results in some alterations in the 3D-network structure, namely in a rearrangement among locally-ordered regions (clusters). Also, a correlation between the loading dependencies of disordered region portion and free volume portion, which have been observed for both the nanocomposites.

7. For both the nanocomposites, different non-monotonous dependences of dielectric permittivity versus the volume portions of clusters or disordered areas unveil differences in mechanisms of oxide-resin interaction and related differences between the nanocomposites in their structural alterations at mesoscale.

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