Cyanate Ester Resin/Silica subnanocomposites and their superiority over nanocomposites due to fundamental role of constrained interfacial dynamics

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Abstract. The study of nanostructure, thermal and relaxation properties (by HAADF-STEM, EDXS, DMA and DSC), combined with the calculations of interparticle distances and interfacial areas, has been performed for a series of the hybrid Cyanate Ester Resin (CER)/SiO₂ polymer composites with 0.01 to 10 wt.% SiO₂ units introduced via a sol-gel process. The absence of clusterization, arising only subnanometric SiO₂ nodes and their quasi-regular distribution within the amorphous matrix, with the shortest distances between nodes, provided their exceptional positive impact on the matrix properties at ultra-low SiO₂ contents of 0.03-0.1 wt.%. The superiority of these subnanocomposites over the nanocomposites was determined by the role of constrained interfacial dynamics over the whole matrix.

1. Introduction

Cyanate Ester Resins (CER) is one of the most important classes of high temperature heterocyclic polymers, with a high crosslink density of triazine cycles in the network [1, 2]. CER have attracted much attention as the matrices of nanocomposites because of their thermal stability up to 400°C, high glass transition temperatures Tg, good fire, radiation and chemical resistance, low water absorption, high adhesion to different substrates and excellent dielectric properties. CER based nanocomposites are widely used as the high temperature structural or functional materials, especially in aerospace field and microelectronics. Amongst these nanocomposites a special place is occupied by materials with the covalently embedded SiO₂ units introduced into the matrix via a sol-gel process [3-7]. In this case, not only the nanocomposites but also, for the first time, polymer subnanocomposites with SiO₂ nodes of L size (0.5 nm < L < 1 nm) could be considered at 0.03-0.1 wt. SiO₂ [5-7].

In this article, we present, alongside with some experimental results, also the results of calculations of such parameters as the average distance d between SiO₂ units in the matrix and the interfacial area S in one cm³ of the composites as the functions of SiO₂ units content and size in the composites. Such approach allowed us to understand the nature of the exceptional, maximally positive impact of ultra-low SiO₂ contents on the composite properties.
2. Experimental part
The CER/SiO\textsubscript{2} composites were synthesized via a sol-gel procedure, from dicyanate ester of bisphenol E (DCBE), tetraethoxysilane (TEOS) and \( \gamma \)-aminopropytrimethoxysilane (APTMS). TEOS was used for formation of SiO\textsubscript{2} units via hydrolysis, followed by condensation of the hydroxyl groups. APTMS was a coupling agent providing reliable covalent embedding of SiO\textsubscript{2} units into the matrix via the reaction of amino groups with cyanate groups (\( \text{−O}−\text{C}≡\text{N} \)). Thus, these composites were synthesized through the reaction of DCBE polymerization into the heterocyclic network, hydrolysis and polycondensation of added silanes into SiO\textsubscript{2} units, and the chemical hybridization of organic and inorganic constituents. The process of preparing the studied composites was described in detail in [5-7]. Figure 1 shows the scheme of CER/SiO\textsubscript{2} hybrid network as found by FTIR spectra [3-5].

![Figure 1](image_url)

**Figure 1.** The scheme of CER/SiO\textsubscript{2} hybrid network with covalently embedded SiO\textsubscript{2} node.

A series of CER/SiO\textsubscript{2} polymer composites with different contents of SiO\textsubscript{2} units, from 0.01 to 10 wt.%, both nanocomposites and subnanocomposites with SiO\textsubscript{2} nodes in the CER network were studied.

The state and distribution of SiO\textsubscript{2} units in the composites were characterized by means of scanning transmission electron microscopy using high-angle annular dark-field (HAADF-STEM) imaging technique combined with energy-dispersive X-ray spectroscopy (EDXS) (Jeol-JEM-2100F microscope, Oxford Instruments INCA EDX spectrometer). EDXS analysis allowed us: (i) to determine Si content in the nanovolumes, even in the cases of no observable SiO\textsubscript{2} clusterization; (ii) to confirm that the STEM observed nanoformations must be attributed to the SiO\textsubscript{2} units; (iii) constructing the maps of Si (i.e., SiO\textsubscript{2} units) distribution in the nanovolumes of composites, and (iii) obtaining the histograms of the statistical distribution of Si content in the composites. Electron beam was focused to spots of ca. 1 nm in diameter with characterization of 1x1x100 nm\textsuperscript{3} volumes, and 10\textsuperscript{2}-10\textsuperscript{3} points were randomly chosen in each composite for the EDX spectra acquisition.

Relaxation dynamics and elastic properties of the composites were estimated over the temperature range from 20° to 350°C by dynamic mechanical analysis (DMA, 1Hz) in tensile mode using a DMS 6100 Seiko Instruments spectrometer, at the heating rate of 2°C min\textsuperscript{−1}. Differential scanning
calorimetry (DSC) with a DSC 6300 Seiko Instruments apparatus was used for estimating $T_g$ at the heating rate of 20$^\circ$C min$^{-1}$.

Alongside with the experiments, the calculations were performed to estimate the interfacial area $S$ ($m^2$) in one cm$^3$ of the composite and the average distance between SiO$_2$ units $d$ (nm) as the functions of SiO$_2$ content introduced and the estimated SiO$_2$ unit sizes. In these calculations, we proceeded from the matrix and SiO$_2$ unit densities of 1.2 g cm$^{-3}$ and 2.1 g cm$^{-3}$ (as for amorphous silica), respectively; and spherical form of SiO$_2$ units.

3. Results and discussion

Figures 2 and 3 show the results of structural analysis of a few composites under study.

![Figure 2](image_url)

**Figure 2.** HAADF-STEM images (a-e) obtained for the CER/SiO$_2$ composites with SiO$_2$ contents of 0.1, 0.5, 1, 2 and 10 wt. %, and Si distribution maps (on the right) obtained by EDX spectroscopy for the composites with 1, 2 and 10 wt. % SiO$_2$.

At 0.1% SiO$_2$, the composite was homogeneous (no nanoclusters) despite the presence of Si in all nanovolumes analysed by EXDS. Therefore, it could contain only SiO$_2$ nodes of subnanometric size as shown in figure 2a. The onset of clusterization could be discerned starting from 0.5% SiO$_2$ in the composite. Nanoclusters of ca. 25 nm in size were present in the nanocomposite with 1% SiO$_2$ but starting from 2% SiO$_2$ nanocluster aggregates were formed in the composites. Their size increased with SiO$_2$ content, from ca. 100 nm to 400 nm in the composites with 2% and 10% SiO$_2$, respectively. The EDXS maps of Si distribution, presented in figure 2 for the composites with 1, 2 and 10% SiO$_2$, proof that the heterogeneities observed in the HAADF-STEM images are related, indeed, to the SiO$_2$ nanoclusters or their aggregates.

Figure 3 represents the histograms of Si content obtained for four composites. Gaussian contours are also shown herein. Their widths are determined by the stochastic nature of the characteristic X-ray
signal generated by the interaction with the electron beam. Therefore, these contours correspond to a hypothetical case of perfectly uniform, quasi-regular distribution of SiO$_2$ units within the matrices, i.e., invariable SiO$_2$ content in all analyzed nanovolumes.

Of special interest is the histogram of the subnanocomposite with 0.1 wt.% SiO$_2$ (no nanoclusters) which practically coincides with the Gaussian contour. That provides the evidence of the quasi-regular distribution of SiO$_2$ nodes in the amorphous matrix network, at the first approximation. Meantime, the substantial deviations of the histograms from the Gaussian contours are observed at 1, 2, and 10 wt. SiO$_2$, as estimated by EDX spectroscopy. Blue Gaussian contours correspond to hypothetical quasi-regular Si distribution in nanovolumes of the composites.

**Figure 3.** Histograms of Si content (at. %) within 1x1x100 nm$^3$ nanovolumes in the CER/SiO$_2$ composites containing 0.1, 1, 2 and 10 wt. SiO$_2$, as estimated by EDX spectroscopy. Blue Gaussian contours correspond to hypothetical quasi-regular Si distribution in nanovolumes of the composites.

DMA and DSC data showed: depending on SiO$_2$ units content, their ambivalent influence on molecular dynamics, thermal, relaxation and elastic properties of CER matrix was revealed. The most positive impact was attained in the absence of nanoclusters, at ultra-low SiO$_2$ contents, e.g., at 0.1% (for subnanocomposite). In this case, the most “suppressive” impact of SiO$_2$ on CER vibrational dynamics was observed already by far-IR spectroscopy [5]. Figures 4 and 5 illustrate this statement by DMA and DSC data. One can see that glass transition temperature, $T_g$, and transition onset
temperature, $T_g'$, increased from 250° and 160°C to 300° and 260°C, respectively. When increasing SiO$_2$ content, the effects decreased, and at 10% SiO$_2$ even negative effects were observed: suppression of dynamics disappeared, and three $T_g$ values, at 100°, 150° and 200°C could be observed (DSC, DMA). Dynamic modulus, $E'$, increased at 20°C from 2 GPa for the neat matrix to 3 GPa for the subnanocomposite [5]. Figure 6 presents the results of calculations showing that at ultra-low SiO$_2$ contents of 0.03-0.1 wt. % in the composites, when clusterization is absent and only subnanometric nodes can be formed and covalently embedded into the matrix network, the anomalously low distances $d = 4$-10 nm and maximal interfacial area $S = 4$ m$^2$ in one cm$^3$ of composite are predicted.

Since the histograms of Si distribution in nanovolumes of these composites indicated the quasi-regular distribution of SiO$_2$ nodes in the matrix, the obtained $d$ values are close to a reality. It means that all atomic groups of the matrix are located at distances not more than 2-5 nm from the points of grafting matrix to SiO$_2$ nodes.

### Figure 4. DMA (1 Hz): mechanical loss factor $\tan \delta$ (T) plots obtained for the neat CER matrix and CER/SiO$_2$ composites with 0.1, 1, 2, 5 and 10 wt.% SiO$_2$.

### Figure 5. Glass transition temperatures, $T_g$s, and glass transition onset temperatures, $T_g'$s, of the CER/SiO$_2$ composites vs. SiO$_2$ content plots by DSC(circles) and DMA (triangles,crosslets)

### Figure 6. The results of calculations of the average distance $d$ between SiO$_2$ units and the interfacial area $S$ in 1 cm$^3$ for the CER/SiO$_2$ composites with different SiO$_2$ contents.
As known, the values of immobilized fragments of grafted polymer chains are determined with the value of Kuhn segment length as a “rigidity element”. Thus, for rigid heterocyclic macromolecules, e.g., for polyimides Kuhn segment is equal to 6-20 nm [8, 9]. For the heterocyclic CER network, the immobilization effect (suppression of mobility, constraining dynamics) may comprise even the network fragments located at larger distances from the points of their tethering to SiO₂ units. It means that in the subnanocomposites with the maximal $T_g$ the whole matrix is in the state of constrained interfacial dynamics (phenomenon of constrained polymer dynamics [10, 11]).

At 0.5-1 wt. % SiO₂, with the onset of clusterization, the interfacial area $S$ dropped down to 1 m² and the distance $d$ increased up to ca. 100 nm. Increasing $d$ to 200 nm may be seen at 2% SiO₂. Finally, at 10 wt.% SiO₂, nanocluster aggregates of 400 nm in size were formed in composites, and $d = 480$ nm (figure 6). Moreover, at 1, 2 and 10% SiO₂ irregular distribution of SiO₂ units in the matrix was registered. This could result also in the wide dispersion of the interparticle distances and, therefore, lead to deterioration of the properties of composites. These estimates suggest the lesser contribution of constraining influence of SiO₂ on the matrix properties. Therefore, the impact of SiO₂ units decreases, becomes negligibly small and even negative due to the elevated defectiveness of network (figures 4, 5).

4. Conclusion
The experimental analysis, combined with some calculations, was performed for a series of hybrid CER/SiO₂ composites with 0.01-10 wt.% SiO₂ synthesized via a sol-gel process. The peculiarities of nanostructure and the ambivalent influence of SiO₂ units on dynamics and properties of these composites were shown. The maximal positive impact of the SiO₂ units was observed at their ultra-low contents of 0.03-0.1 wt.%: The experiments and calculations lead to the conclusion that it is explained by the subnanocomposite nature of these materials, quasi-regular distribution of SiO₂ units in the amorphous matrix and the controlling role of the constrained interfacial dynamics peculiar to the whole matrix of the subnanocomposites.

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