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Chemical ensuring subnanostructures formation in densely crosslinked organic-inorganic hybrid polymer networks

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Cyanate Ester Resins are known to form polymer networks through reaction of polycyclotrimerization of cyanate groups. Cyanate groups are highly reactive towards active hydrogen containing organic groups as well. The high crosslink density organic-inorganic hybrid polymer networks have been synthesized from the mixture of tetraethoxysilane (TEOS), 3-aminopropyltrimethoxysilane (APTMS) and 1,1-Bis(4-cyanophenyl)ethane (DBCE). First, acid hydrolysis of the silanes followed by polycondensation reaction of the hydrolysis products was fulfilled in situ, and then reaction of DBCE cyanate groups with amino and hydroxyl groups of silica units formed was carried out under mild conditions. As a result, some DCBE molecules appeared to be chemically grafted to the silica network units. Then, polycyclotrimerization of DCBE free and grafted (by one side) molecules was performed at high temperatures. The composites with silica contents from 0.01 to 10 wt. % were prepared. The state of silica in the composites has been characterized by means of FTIR, high-angle annular dark-field scanning transmission electron microscope (STEM) combined with Energy-dispersive X-ray spectroscopy (EDXS). For the composites with ultralow silica contents (<<1 wt. %), the structures without nano- or microclusters but with silica units distributed quasi-regularly within the amorphous polymer matrix have been formed. The data obtained imply the existence only in this case of subnanometer-sized silica nodes connected covalently with the matrix, i.e., the formation of the hybrid subnanocomposites. The Far-IR spectroscopy, DMA (Dynamic Mechanical Analysis) and DSC (Differential Scanning Calorimetry) data showed that these subnanocomposites manifest the largest "constrained dynamics" effect and superiority in thermal and mechanical properties compared to those of the nanocomposites with higher silica contents containing nanoclusters and their aggregates.

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