Ultra-heat resistant nanocomposites based on heterocyclic networks: structure, properties, origin of thermal stability

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Abstract. A series of the hybrid Bisphenol A based Phthalonitrile (BAPhN)/amino-Montmorillonite (amino-MMT) polymer nanocomposites with the complex heterocyclic matrix network and 0.03–5.0 wt.% amino-MMT were synthesized and studied. Their molecular structure, nanostructure, molecular dynamics, thermal, relaxation and elastic properties were characterized using TEM, EDXS, DMA, TGA, FTIR and Far-IR spectroscopies including also the experiments in flowing nitrogen medium. Depending on nanofiller content, different extents of MMT stacks exfoliation, from a single nanolayer to stacks with tens nanolayers-thickness, were registered in these nanocomposites. The exceptional combining of high temperature properties was revealed for these nanocomposites.

1. Introduction
Demand for polymeric materials with high thermal stability continues to be increasingly important in some fields, for instance, in aircraft, space and marine structures, in “hot zones” of different constructions and in microelectronics. Keller with co-workers synthesized for the first time the densely crosslinked heterocyclic phthalonitrile network polymers [1, 2], and in recent years the composites based thereon have taken a leading position as the polymer materials for the applications at temperatures of 300-400°C [3]. Amongst the inorganic nanoparticle for obtaining polymer nanocomposites a special position occupy 2D silicate nanolayers with about 1 nm in thickness obtained via splitting (exfoliation) of mineral montmorillonite (MMT) blocks in polymer matrix. This is due to a high aspect ratio of 2D nanolayers, their good properties, accessibility and low cost. Recently, we have performed the combined research of molecular structure, nanostructure and properties of phthalonitrile nanocomposites with different contents of organo-modified MMT nanolayers [4-6].

2. Experimental part
Nanocomposites were synthesized from monomer Bisphenol A Phthalonitrile (BAPhN) with 0.03-5.0 wt. % amino-modified montmorillonite (amino-MMT 1.30E) via curing by step by step at 260-300°C. As shown by IR spectroscopy [4], the curing regime used resulted in only a partial polymerization of BAPhN. Therefore, post-curing procedures were also performed at temperatures from 340° to 530°C which allowed increasing polymerization degree up to 95%. The films of 0.5 mm thickness have been used.
The state and distribution of MMT nanolayers in the nanocomposites were characterized by means of transmission electron microscopy (TEM) combined with energy-dispersive X-ray spectroscopy (EDXS) (Jeol-JEM-2100F microscope, Oxford Instruments INCA EDX spectrometer). EDX spectra were obtained using electron beam focused to spots of ca. 2 nm in diameter. The application of EDXS in addition to TEM allowed us direct verification of observed structural features nature and controlling local elemental composition (Si, Al and Mg elements) in the sample nanovolumes including the presence of single 1-nm thickness MMT nanolayers in the nanocomposites.

Relaxation dynamics and elastic properties of the nanocomposites were estimated by dynamic mechanical analysis (DMA, 1Hz) in the tensile mode using a DMS 6100 Seiko Instruments spectrometer, at heating from 20° to 570°C in air or flowing nitrogen mediums, with the rate of 3°C min\(^{-1}\). Two heating cycles were carried out typically for each sample: the first cycle from 20° to 430°C characterized the properties of initially cured composites. During the second heating cycle, from 20° to 570°C, the characteristics of post-cured samples were estimated.

IR spectroscopy (IRS) was used for getting the information on molecular structure of the nanocomposite matrix, polymerization control, and the changes in the matrix molecular dynamics caused by both post-curing and the incorporated MMT nanoparticles. FTIR spectra were recorded using a Bruker model Tensor 37 spectrometer, and far-IR spectra were registered using a FIS-21 Hitachi spectrometer. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were applied using a TGA Q50 TA Instruments under both air and inert (flowing nitrogen) atmospheres, at heating from 20 to 900°C with the heating rate of 20°C min\(^{-1}\).

3. Results and discussion

IR spectra indicated the complex molecular structure of the BAPhN based heterocyclic matrix network including the phthalocyanine, triazine and isoindoline fragments (figure 1), however, the phthalocyanine ones prevailed in the network structure as it was shown by far-IR spectra [4].

Figure 1. The molecular formulas of monomer and three basic fragments constituting the complex heterocyclic matrix network.

Depending on the MMT content in the nanocomposites, very different levels of exfoliation of 2-D silicate MMT stacks within the amorphous matrix were registered by TEM and validated by EDXS. Thus, from a single nanolayer to two-three-layer formations were observed, at 0.03-0.5 % MMT.
Figure 2. TEM micrographs of the BAPhN based nanocomposites with 0.1, 0.5, 1 and 5 wt.% amino-MMT.

Figure 3. EDX spectra of the BAPhN/amino-MMT nanocomposites taken from 2 nm spots in diameter at focusing electron beam at polymer matrix (with small involving MMT), at single MMT nanolayer or at MMT stack. Signal from Cu is not related to the sample.

Different degrees of MMT exfoliation, including simultaneously the single nanolayers, thin stacks consisting from a few nanolayers, and the stacks of 5-10 nm thickness were registered in the case of 1%MMT in the nanocomposite. And only “thin” and “thick” MMT stacks of 5 nm and 20-30 nm in thickness, respectively, were registered at 2% and 5% MMT in the composites (figure 2). The EDX spectra, using electron beam focused to 2 nm spots, allowed us tracking the basic features observed in the TEM images, including a single 1 nm thickness MMT nanolayer (figure 3).

Our far-IR spectroscopy measurements [4, 5] indicated the basic contribution of phthalocyanine heterocycles to the structure of the BAPhN based matrix network. Moreover, introducing the reactive amino-MMT nanolayers and post-curing procedure resulted in discernable changes in the far-IR spectrum: a decrease in absorption bands intensities and the displacement of the peak maxima to higher wave numbers. These spectral changes corresponded to the effect of some constraining network dynamics (see, e.g., about the phenomenon of constrained dynamics in [7, 8]).

DMA results showed that at the first scanning up to 430°C glass transition temperature $T_g$, as estimated by $\tan\delta$ peak maximum temperature, equaled 380–390°C for both neat BAPhN matrix and the studied nanocomposites. However, after post-curing procedure by heating up to 430°C the relaxation spectra changed dramatically (figure 4). A single glass transition peak with $T_g = 446°C$ for the post-cured neat BAPhN matrix but the dissimilar, depending on the MMT content, and complicated spectral contours were observed for the nanocomposites. They show arising of the pronounced dynamic heterogeneity in the glass transitions; it was most pronounced for the composite with 1% MMT and turned out to be in a good accordance with the nanostructural data (figure 2). On the whole, from figure 4 one can see the different “constrained dynamics” effects. This figure indicates the presence of matrix nanovolumes with relatively slight influence of MMT on the post-cured matrix (with $T_g \approx 460°C$) and “constrained dynamics” effects in composite nanovolumes providing $T_g \approx 470$, 500, 520, 530-540 or even 570°C.
Figure 4. DMA, 1Hz. The relaxation spectra obtained for post-cured samples of the neat BAPhN matrix and BAPhN based nanocomposites with 0.03, 0.1, 0.5, 1 and 5 wt.% amino-MMT.

Figure 5 demonstrates the revealed unusual (for polymers) effect. It shows the DMA data, $\tan(\delta)(T)$ and dynamic modulus $E'(T)$ plots, obtained for the cured BAPhN/amino-MMT(0.5 wt.%) nanocomposite at the scanning in air medium up to 430°C and rescanning in nitrogen medium after heating in this inert environment up to 570°C. One can see the complete suppression of the relaxation spectrum, the disappearance of the glass transition and the practically constant value of modulus $E'$ = 3 GPa in the temperature range from 20° to 600°C.

Figure 6 illustrates thermal stability and thermo-oxidative degradation of the neat matrix and two nanocomposites as studied using TGA and DTG analyses under air atmosphere and in inert (N₂).
medium at temperatures between 20° and 900°C. Slight thermal degradation starts from ca. 430°C. At this early stage the process does not depend on the medium up to 550°C when about 20 % mass is lost although the films retain the satisfactory integrity. However, from 550°C as “the temperature bifurcation point”, TGA curves obtained in air and nitrogen mediums sharply diverge due to “switching on” the thermo-oxidative process in air medium. Char residues at ~ 700°C were equal to 7 and 73 wt. % in air and N₂, respectively.

Two points must be noted herein. First, after heating up to 900°C in inert atmosphere nanocomposites retained the satisfactory integrity, and their char residues were equal to ca. 70%. And, secondly, incorporating MMT nanolayers resulted in increasing thermo-oxidative stability in air medium, and char residues at ~ 700°C were equal to 7 and 45 wt.% for the neat matrix and nanocomposite, respectively (figure 6). The latter effect could be explained by the barrier effect, the changes in degradation kinetics, suppression dynamics in the matrix, etc.

The origin of ultrahigh thermal properties of these nanocomposites consisted in the basic role of phthalocyanine heterocycles in the molecular structure of matrix network and in chemical grafting of amino-MMT nanofiller to the polymer matrix. After heating the BAPhN/amino-MMT nanocomposite up to 900°C with the rate of 20°C /min in nitrogen atmosphere (TGA experiment), retaining the material integrity was observed, and the characteristic changes in its FTIR spectrum were as follows: the intensities of absorption bands at 1360 cm⁻¹ and 1520 cm⁻¹ (triazone cycles), and 1503 cm⁻¹ (isoindoline cycles) sharply decreased, whereas the intensities of absorption bands at 1010 cm⁻¹ (displaced to 1028 cm⁻¹) and 3450 cm⁻¹ (phthalocyanine cycles) considerably increased (figure 7).
Figure 7. IR spectra of the cured BAPhN/amino-MMT (5 wt.%) nanocomposite before (green line) and after heating up to 900°C in nitrogen medium (purple line)

This result led to conclusion that at high temperature pyrolysis the destruction of triazine and isoindoline cycles occurred, with their partial transformation into stable phthalocyanine heterocycles.

4. Conclusion

The complex physical research of the structure, dynamics and properties of the BAPhN/amino-MMT nanocomposites has been performed. The pronounced dynamic heterogeneity in the glass transition, the different “constrained dynamics” effects and positive impact of MMT additive on thermal stability of the nanocomposite at $T > 500^\circ$C in air medium were shown. The unique (for polymers) combination of high temperature properties could be attained for these nanocomposites including (a) practically invariable modulus $E' = 3$ GPa over the temperature range from 20° to 600°C; (b) increasing $T_g$ up to 570°C, and (c) the satisfactory thermal stability, with retaining the material integrity, at short-term heating to 500°C in air medium or up to 900°C in oxygen-free medium. These nanocomposites may be considered as promising materials for application under the extremal conditions.

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