



SYNTHESIS AND STRUCTURE-PROPERTIES RELATIONSHIP FOR NANOCOMPOSITES BASED ON THERMOSTABLE POLYCYANURATE NETWORK AND MONTMORILLONITE

Alexander M. Fainleib^{*}, Iryna M. Bei^{*}, Panayitis Maroulas^{**}, Sotiria Kriptou^{**}, Polycarpos Pissis^{**},
Vladimir A. Bershtein^{***}, Yurii P. Gomza^{*}, Pavel N. Yakushev^{***}

^{*}Institute of Macromolecular Chemistry of National Academy of Sciences, Kyiv, Ukraine

^{**}National Technical University, Department of Physics, Athens, Greece

^{***}Ioffe Physico-Technical Institute of the Russian Academy of Sciences, St Petersburg, Russia

Keywords: *nanocomposite, polycyanurate, montmorillonite*

Abstract

Polycyanurate-based nanocomposites filled with organically treated montmorillonite were synthesised and investigated. The results of the kinetics study have shown that the aluminosilicate filler acts as a catalyst and promotes monomer conversion. The structure of the montmorillonite in the polymer matrix investigated by WAXS and TEM was defined as partly intercalated/exfoliated. At the same time combined analysis by means of DSC and creep rate spectroscopy allowed us to conclude that introduction of inorganic filler into PCN matrix results in formation of complex nanosized morphology. DRS results have revealed reduction of molecular mobility of the PCN in the nanocomposites obtained. The latter provides a basis for discussing the improvement of barrier, mechanical and thermal properties at a molecular level.

1 Introduction

Polycyanurates based on cyanate ester resins are among the most promising engineering polymers due to their unique combination of physical properties (flame resistance, low water uptake, dimensional and thermal stability, high glass transition temperature, low dielectric loss) [1]. To eliminate the main drawback of high crosslink density polycyanurate networks (PCN) – brittleness – they are combined with rubbers, thermoplastics, polyethers, polyesters, polyurethanes [1, 2]. Using of flexible-chain oligomers or polymers for modification of polycyanurates has allowed

improving of mechanical performance of the latter, but at the expense of thermal stability. An introduction of inorganic nanofillers into PCN-based matrix could be helpful approach to solve this problem. In the present work new polycyanurate/montmorillonite (MMT) nanocomposites were synthesized and the kinetics peculiarities of their synthesis, structure and molecular mobility were investigated and discussed.

2 Experimental

The polycyanurate matrix used in this study was synthesized from dicyanate ester of bisphenol A (DCBA), supplied by Novocheboksarsk, Russia. Two types of MMT (common trade name Cloisite) from Southern Clay Products, USA, were investigated. Natural unmodified Na-MMT (Cloisite Na) and organically treated MMT Cloisite 30B (modified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium) were used as received.

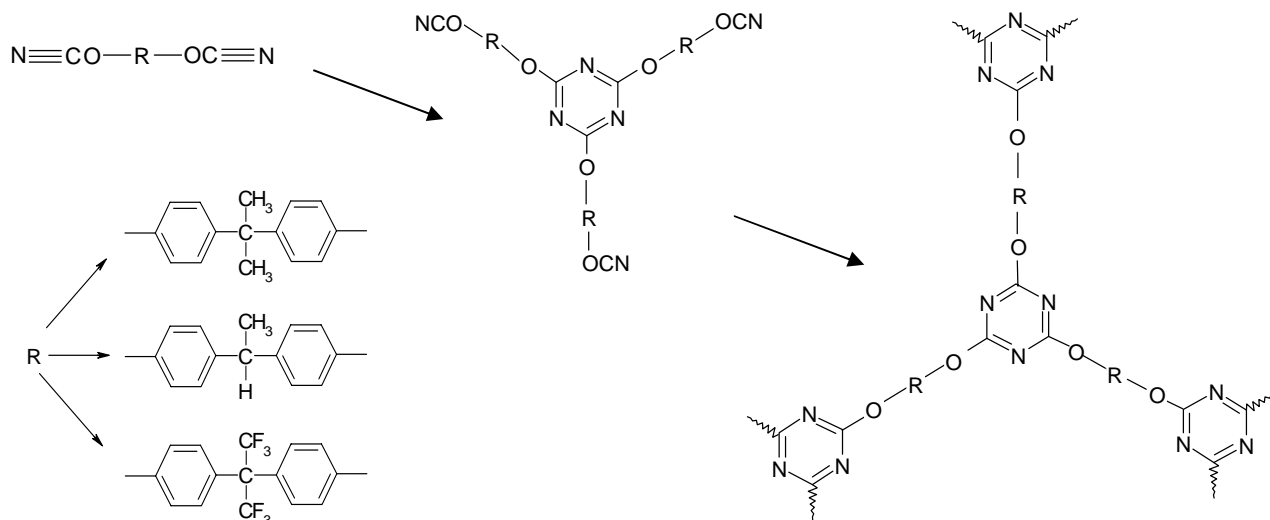
PCN/MMT nanocomposites were synthesized by the following way: the required amounts of DCBA and MMT were dissolved in acetone at room temperature. To provide a better dispersion of MMT in a polymer matrix an ultrasonic (US) treatment at 22 kHz during 5 min was applied. Solvent was removed by distillation at 100°C under vigorous stirring. All compositions were degassed under vacuum before curing. Curing schedule for all systems was as follows: 5h at 150°C, then 3h at 180°C and then 1h at 210°C.

The composites obtained were investigated by means of IR-spectroscopy, sol-gel analysis, WAXS, TEM, DSC, DRS, creep rate spectroscopy (CRS).

Synthesis and structure-properties relationship for nanocomposites based on thermostable polycyanurate network and montmorillonite

3 Results and discussion

3.1 PCN formation



The process of DCBA polymerization reveals at the IR-spectra (see Fig. 1) in reducing (up to total disappearance in fully cured network) of O-C≡N characteristic doublet band ($2240 - 2270\text{ cm}^{-1}$). Moreover, PCN-formation is accompanied by the appearance and intensity increasing of two absorption bands at 1570 and 1370 cm^{-1} as a consequence of transformation of C≡N-groups (DCBA) into C=N-groups (triazine rings of PCN).

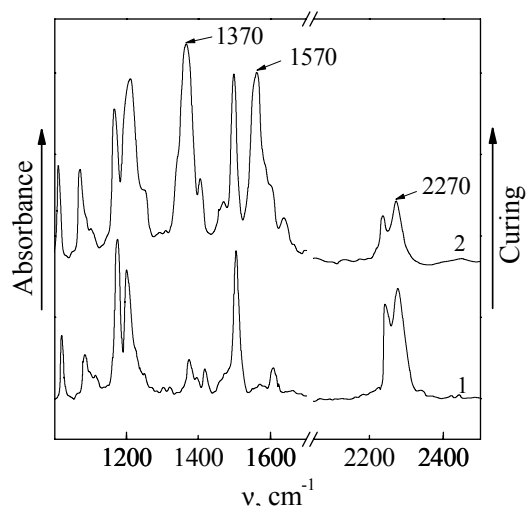


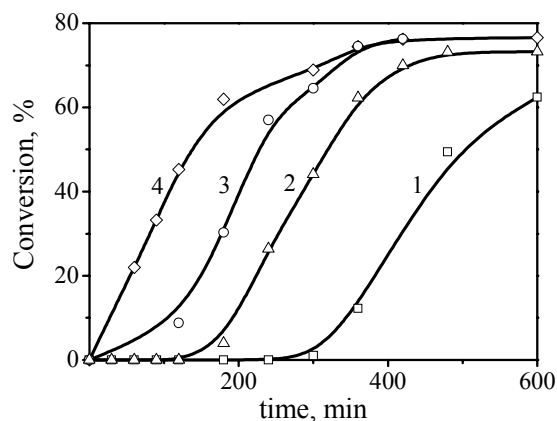
Fig. 1. IR-spectra of the initial DCBA (1) and PCN with an intermediate conversion degree (2)

Kinetics peculiarities of isothermal curing of DCBA in the presence of MMT at 150°C were

Dicyanate esters can undergo thermal or catalytic polycyclotrimerization (an addition process) resulting in three-dimensional polycyanurate network as shown below:

studied using IR-spectroscopy technique. Neat DCBA, DCBA/Cloisite Na (98/2), DCBA/Cloisite 30B (98/2) and (95/5) were chosen for the kinetics experiment to reveal effect of the clay nature as well as concentration of the organically treated MMT on the PCN-formation. Conversion of the monomer was calculated from the intensity decreasing of the absorption band at 2270 cm^{-1} (absorption band of CH_3 -groups stretching vibrations at 2970 cm^{-1} was used as a standard).

“Conversion vs. time” dependences for the systems under investigation are shown in Fig. 2.



MMT content (wt.%): 1 – 0; 2 – 2% Cloisite Na; 3 – 2% Cloisite 30B; 4 – 5% Cloisite 30B

Fig. 2. Effect of MMT on polymerization of DCBA

As one can see, introduction of the unmodified Na-MMT into the monomer results in simultaneous reducing of the reaction induction time and increasing of the conversion rate compared to the neat DCBA curing process. The replacement of the Na-ions situated in the galleries of the natural MMT by the alkylammonium cations leads to the additional acceleration effect on polymerization of DCBA.

This “catalytic” effect of MMT on DCBA polymerization process can be explained in the following way. It should be noted that DCBA can react with hydroxyl groups of the MMT surface modifier or water traces forming carbamates. The latter, in its turn, accelerates formation of the polycyanurate network [1]. On the other hand polycyclotrimerization of DCBA can be affected by metal cations such as Al³⁺ and Fe³⁺ [1,3], situated on the MMT surface as a result of isomorphous substitutions and/or lattice imperfection [4,5].

To determine the part of the monomer involved in the polycyclotrimerization reaction a sol-gel analysis in boiling acetone was performed. Gel-fractions found for all composites under investigation vary from 99,1% to 99,9%, indicating that practically all DCBA participates in polycyanurate network formation.

3.2 Structure of the PCN/MMT nanocomposites

WAXS analysis is usual approach to study the structure of the clay in polymer nanocomposites. The spacing between two silicate layers of MMT can be calculated according to Bragg’s law (eq. 1):

$$d = \lambda / (2 \sin \theta) \quad (1)$$

where d – the spacing between diffractive lattice planes, λ corresponds to the wave length of the X-ray radiation used in the diffraction experiment, and θ is the measured diffraction angle.

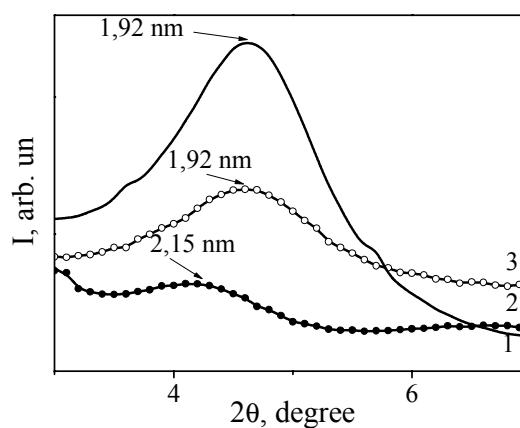
Structure parameters of the composites under investigation are summarized in Table 1.

Table 1. Structure parameters of PCN/MMT nanocomposites

Specimen (wt.%)	2 θ , deg	d , nm
MMT (Cloisite 30B)	4,6	1,92
PCN/Cloisite 30B (98/2)	3,9	2,26
PCN/Cloisite 30B (97/3)	4,2	2,10
PCN/Cloisite 30B (96/4)	4,2	2,10
PCN/Cloisite 30B (95/5)	4,1	2,15

In PCN-based nanocomposites the main diffraction peak of Cloisite 30B shifts towards the lower angle values indicating intercalation of the clay [4,5]. At the same time regular changing of its intensity comparing to the neat Cloisite 30B was observed. This phenomenon could be treated from both concentration decreasing effect and disordering of the clay stacks as a result of the exfoliation. To verify the last assumption “mechanical blends” of the ground cured PCN and proper amounts of MMT were obtained and their X-ray diffraction patterns were registered (see Fig. 3 as an example).

The “mechanical blend” is a model of the PCN/MMT system supposing an absence of interaction between the components and correspondingly changes in the structure of the MMT inside polycyanurate matrix (curve 3 in Fig. 3). In this case the 2 θ -position of the Cloisite 30B peak still the same as for the neat clay. The obvious difference in the peaks area of curves 2 and 3 indicates decreasing of the contribution of well-ordered MMT fraction to total wide-angle X-ray diffraction pattern owing to clay delamination. These results allow us to suppose the structure of the nanocomposites synthesized as partly intercalated/exfoliated.



1- Cloisite 30B; 2- nanocomposite; 3- mechanical blend

Fig. 3. WAXS patterns of PCN/Cloisite 30B (95/5) systems

An obvious illustration of the nanocomposites structure can be obtained using TEM technique. Fig. 4 shows a typical microphotograph of the PCN containing 5 wt.% of Cloisite 30B.

The dark lines in Fig. 4 represent individual sheets of Cloisite 30B with thickness about 1 nm. As one can see statistically distributed discreet plates as

Synthesis and structure-properties relationship for nanocomposites based on thermostable polycyanurate network and montmorillonite

well as well-organized stacks of MMT present simultaneously in the polycyanurate matrix.

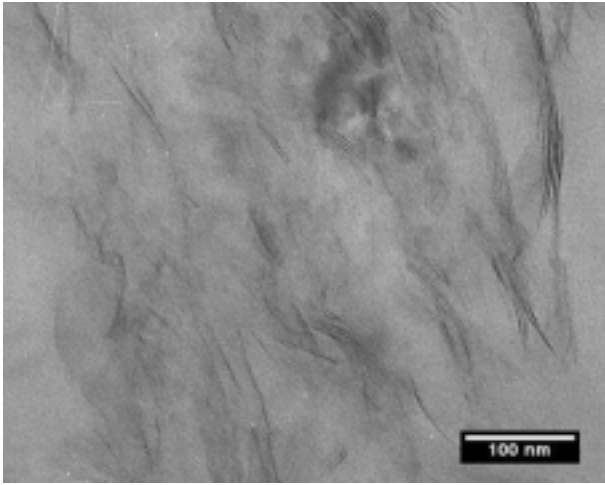


Fig. 4. TEM image of PCN/Cloisite 30B (95/5)

Thus our suggestion about complex intercalated/exfoliated structure of the PCN/MMT composites based on the WAXS analysis has got an additional proof from TEM.

3.3 DSC measurements

To prevent any possibility of the postcuring process development during DSC experiments, samples of PCN/MMT composites were stabilized in order to attain the total CN→PCN conversion. The optimal conditions for thermal treatment chosen after a number of preliminary experiments were as follow: 20 min treatment at 270 °C, then heating to 330 °C with immediate cooling in a calorimeter.

Table 2 represents glass transition temperatures of PCN/MMT composites derived from DSC curves, registered at heating rate of 20 °C/min.

Table 2. Plurality of T_g in PCN/Cloisite 30B nanocomposites

MMT content (wt.%)	Ultrasonic treatment	Glass transition 1*			Main glass transition 2		Glass transition 3	
		T_g , °C	T_g , °C	ΔC_p , J/g·°C	T_{g2} , °C	ΔC_p , J/g·°C	T_{g3} , °C	ΔC_p , J/g·°C
0	—	—	—	—	284	—	—	—
2	—	46	144	0.07	279	0.21	377	0.09
2	+	58	145	0.08	287	0.25	375	0.11
5	+	42	138	0.07	273	0.25	377	0.13

* where T_g , T_g onset and end of the broad glass transition respectively

Unlike DSC curve for completely crosslinked pure PCN with one glass transition and $T_g = 284$ °C three glass transitions can be observed by DSC for PCN-MMT nanocomposites (see Table 2) including the main glass transition T_{g2} corresponding to that in pure PCN; slight but broad transition at T_{g1} at moderate temperatures of ~ 30 – 130 °C, and glass transition $T_{g3} \approx 380$ °C directly preceding to the onset of decomposition exotherm.

Similar glass transition plurality in PCN-based systems was discovered and described in our previous works [6-8]. This phenomenon was referred to the presence in the PCN matrix of nanodomains with different cross-linking degree. Such conclusion was based on “one-to-one” relationship for T_g vs. conversion degree (X) observed in thermosetting systems including polycyanurates [9,10].

Thus DSC results for PCN/MMT composites may tentatively be interpreted, in our opinion, in a following way. Introducing 2 – 5 % of Cloisite nanolayers did not affect the majority of PCN nanodomains (the “usual” main glass transition T_{g2})

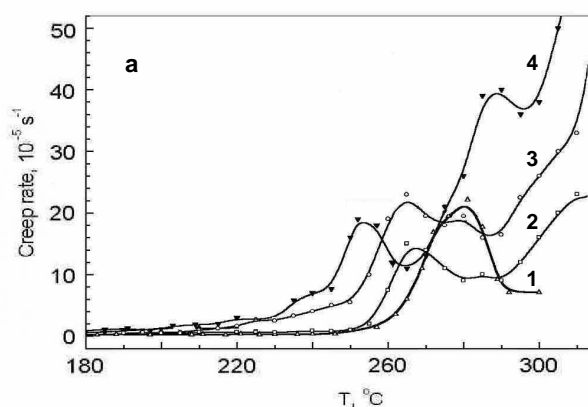
but prevented total CN→PCN conversion in some PCN nanodomains (transition 1, $X_{CN \rightarrow PCN} \approx 0.65-0.80$ [7]). On the other hand, in PCN nanodomains close to silicate nanolayers the effect of constrained dynamics took place. “Unfreezing” dynamics in these domains could occur due to irreversible destroying PCN-MMT interaction at temperatures $T \geq 330$ °C (non-cooperative transition 3), before the onset of decomposition process.

3.4 Creep rate spectroscopy

Creep rate spectroscopy (CRS), as a technique for relaxation spectrometry and thermal analysis, has been developed and successfully used at the Ioffe Institute (St Petersburg, Russia). It consists of precise measuring of creep rates at a constant (typically low) stress as a function of temperature by use of a laser interferometer based on the Doppler Effect. The CRS setups, operating under uniaxial tension or compression, and experimental technique have been described elsewhere [11-13]. The CRS technique manifested superior resolution in

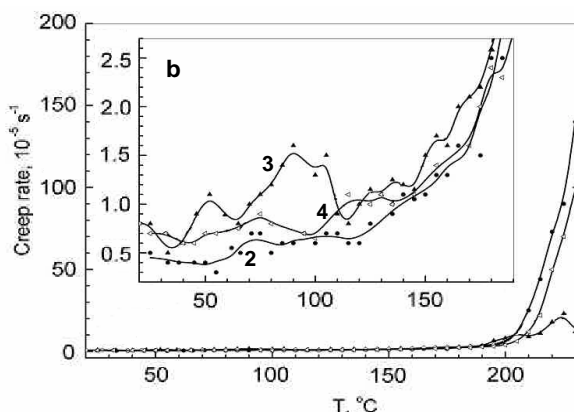
comparison with conventional relaxation spectrometry methods.

The creep rate spectra measured over the temperature range from room temperature to over 300°C are presented in Fig. 5. The choice of the maximum stress (10 MPa) at low temperatures was conditioned with the capability of inducing sufficient creep rates to be measured. At elevated temperatures the low tensile stress of 0.5 MPa was sufficient to maintain a high spectral resolution



without distortion and smoothing out of a spectral contour and preventing a premature rupture of a sample.

As it was revealed before by means of DSC, high resolution creep rate spectra, obtained either at low stress and elevated temperatures, or at increased stress and low temperatures show pronounced heterogeneous nature of glass transition dynamics of PCN/MMT nanocomposites.



1 – PCN; 2 – PCN/Cloisite 30B (98/2); 3 – PCN/Cloisite 30B (98/2) without US treatment; 4 – PCN/Cloisite 30B (95/5)

Fig. 5. Creep rate spectra of PCN/Cloisite 30B composites measured at 0,5 MPa (a) and 10 MPa (b)

One can see a single glass transition 2 for pure PCN (Fig. 5a) but more complicated glass transition dynamics for the nanocomposites. Slightly increasing of creep rates at 200 – 250 °C and simultaneous slight decreasing of T_{max} for glass transition 2 take place owing to introduction of the clay into PCN. It should be noted that creep rate spectra measured at high temperature and small stress of 0,5 MPa were broken off at temperatures over 300 °C due to fracture of the samples. Nevertheless, arising of some components at higher temperatures, ~ 290 and 310 °C, in the region of glass transition 3 is evident.

Fig. 5b shows that creep rate spectra obtained at moderate temperatures and tensile stress of 10 MPa (see insert) confirm slight manifestation of glass transition 1 in PCN/MMT (98/2) composite, synthesized without US treatment.

With some assumptions, a “dispersion” of glass transition temperatures in the PCN/MMT composites could be treated in the framework of the presence of nanodomains with different densities of rigid crosslinking (conversion $X_{CN \rightarrow PCN}$) in the filled PCN network. As a result, CRS data allowed estimating not only the dynamic heterogeneity but

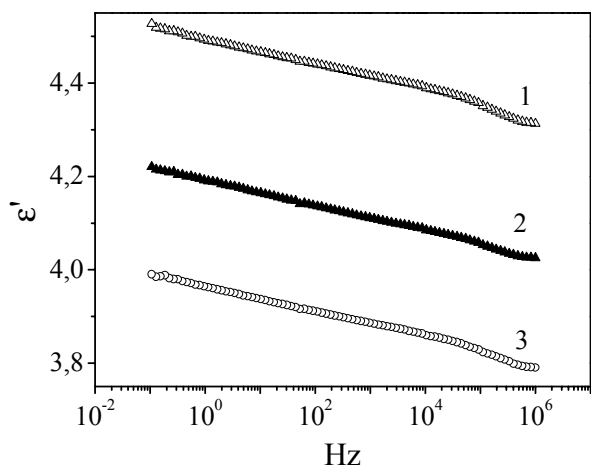
also the compositional nanoheterogeneity in these networks.

3.5 DRS at room temperature

In this work broadband dielectric relaxation spectroscopy in the frequency range of 0.1 Hz to 1 MHz at room temperature was used. Due to the fact that the real part of dielectric function (ϵ') is a measure of polarizability at the temperature and frequency of measurement, DRS technique allowed us to receive information about molecular mobility in PCN/MMT composites. Fig. 6 represents effects of the ultrasonic treatment as well as MMT content on the molecular mobility of polycyanurate. It was established that the real part of permittivity (ϵ') decreases when ultrasonic treatment is applied to disperse the clay in the monomer. We assumed that this decreasing ϵ' is related to better exfoliation of MMT in the polymer matrix resulting in reduction of molecular mobility of polycyanurate [5].

The same effect is observed with addition of larger amount of exfoliating MMT (see curve 3 in fig. 6), supporting the opinion that exfoliation results in reduction of molecular mobility.

Synthesis and structure-properties relationship for nanocomposites based on thermostable polycyanurate network and montmorillonite



1 – PCN/Cloisite 30B (98/2) without US treatment; 2 – PCN/Cloisite 30B (98/2); 3 – PCN/Cloisite 30B (95/5)

Fig. 6. DRS measurement at room temperature of PCN/Cloisite 30B composites

It is therefore believed that inclusion of MMT in the polymer network of PCN reduces its molecular mobility, providing a basis for discussing the improvement of barrier, mechanical and thermal properties at a molecular level.

3.6 Mechanical properties

A laser interferometer was also used for precisely measuring the modulus of elasticity, estimated at tensile stress as a function of temperature, for neat PCN as well as PCN/MMT composites under study.

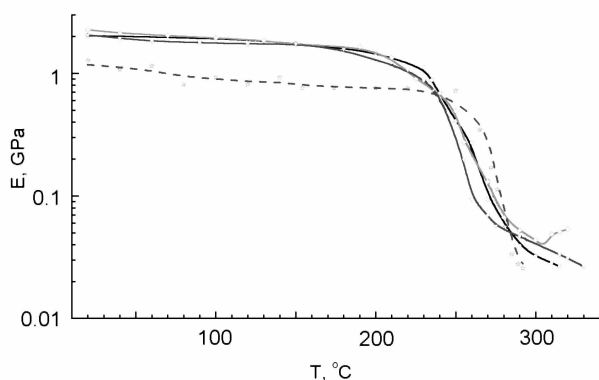


Fig. 7. Elastic modulus of PCN (dotted line) and PCN/MMT composites (solid lines)

It was established that introduction of the MMT in polycyanurate results in increasing elastic modulus at temperatures below 250 °C. No sufficient effect of either the ultrasonic treatment no MMT concentration was detected for the

nanocomposites under study in this temperature interval comparing to the neat PCN.

Acknowledgements

We would like to thank Florent Dalmas, Institut de Chimie et des Matériaux Paris-Est (ICMPE), Thiais, France for providing TEM analysis.

References

- [1] Hamerton I, editor. “*Chemistry and Technology of Cyanate Ester Resins*”. 2nd edition, Chapman & Hall, Glasgow, 1994.
- [2] Fainleib A., Grigoryeva O., Pissis P. Modification of Polycyanurates by Polyethers, Polyesters and Polyurethanes. Hybrid and Interpenetrating Polymer Networks, in “*Focus on Natural and Synthetic Polymer Science*”, C. Vasile, G.E. Zaikov, editors. Nova Science Publishers, Inc., New-York, 2006, p. 49-84.
- [3] Nair C. P. R., Mathew D., Ninan K. N. “Cyanate ester resins, recent developments”. *Adv. Polym. Sci.*, Vol. 155, pp. 1-99, 2000.
- [4] Utracki L.A. “*Clay-containing polymeric nanocomposites*”. Rapra technology Ltd., Shrewsbury, 2004.
- [5] Pinnavaia T.J., Beall G.W., editors. “*Polymer-clay nanocomposites*”. John Wiley & Sons Ltd., Chichester, 2000.
- [6] Bershtein V.A. Egorova L.M., Ryzhov V.A., Yakushev P.N., Fainleib A.M., Shantalii T.A., Pissis P. “Structure and segmental dynamics heterogeneity in hybrid polycyanurate-polyurethane networks”. *J. Macromol. Sci.-Physics*. Vol. B40, No 1, pp. 105-131, 2001.
- [7] Bershtein V.A. David L., Fainleib A.M., Grigoryeva O.P., Bey I.M., Yakushev P.N. “Structural/compositional nanoheterogeneity and glass transition plurality in amorphous polycyanurate-poly(tetramethylene glycol) hybrid networks”. *J. Polym. Sci. Part B: Polym. Phys.*, Vol. 43, pp. 3261-3272, 2005.
- [8] Bershtein V.A. Egorov V.M., Yakushev P.N., David L., Fainleib A.M., Grigoryeva O.P., Bey I.M., Kriptomou S., Pissis P. “Structure and dynamic/compositional heterogeneity in amorphous polycyanurate-poly(tetramethylene glycol) hybrid networks”. *J. Macromol. Sci., Part B: Polym. Phys.*, Vol. 46, No 1, pp. 207-230, 2007.
- [9] Georjon, O., Galy, J., Pascault, J. P. “Isothermal curing of an uncatalyzed dicyanate ester monomer : kinetics and modeling”. *J. Appl. Polym. Sci.* Vol 49, No 8, pp. 1441-1452, 1993
- [10] Lin R.-H., Su A.-Ch., Hong J.-L. “Glass transition temperature versus conversion relationship in the polycyclotrimerization of aromatic dicyanates”. *Polym. Int.* Vol. 49, pp. 345-357, 2000.

- [11]Peschanskaya N.N., Yakushev P.N., Sinani A.B., Bershtein V.A. "New possibilities for the study of deformation kinetics and relaxations in polymers using a laser interferometer". *Thermochim. Acta*. Vol. 238, pp. 429-452, 1994.
- [12]Peschanskaya N.N., Yakushev P.N., Sinani A.B., Bershtein V.A. "Creep rate spectroscopy using a laser interferometer as ultra-high resolution technique for study of relaxations". *Macromol. Symp.* Vol. 119, pp. 79-87, 1997.
- [13]Bershtein V.A., Yakushev P.N., Peschanskaya N.N. "Creep rate spectroscopy: High-resolution analysis of relaxations and prediction of anomalies in mechanical behavior of solids". *Macromol. Symp.* Vol. 147, pp. 73-82, 1999.