



**HAL**  
open science

# **Curing Kinetics of Cyanate Ester Resin in the Presence of Different Inorganic Nanoparticles and Thermal Properties of the Nanocomposites Synthesized**

Diana Shulzhenko, Olga Starostenko, Olga Grigoryeva, Laurent Michely,  
Alexander Fainleib, Daniel Grande

## ► To cite this version:

Diana Shulzhenko, Olga Starostenko, Olga Grigoryeva, Laurent Michely, Alexander Fainleib, et al.. Curing Kinetics of Cyanate Ester Resin in the Presence of Different Inorganic Nanoparticles and Thermal Properties of the Nanocomposites Synthesized. IEEE 12th International Conference Nanomaterials: Applications & Properties (NAP 2022), Sep 2022, Cracovie, Poland. <10.1109/NAP55339.2022.9934391>. <hal-03938814>

**HAL Id: hal-03938814**

**<https://hal.science/hal-03938814v1>**

Submitted on 3 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Copyright - All rights reserved

# Curing Kinetics of Cyanate Ester Resin in the Presence of Different Inorganic Nanoparticles and Thermal Properties of the Nanocomposites Synthesized

Diana Shulzhenko  
*Institute of Macromolecular Chemistry  
of the NAS of Ukraine*  
Kyiv, Ukraine  
shulzhenko\_d@nas.gov.ua

Olga Starostenko  
*Institute of Macromolecular Chemistry  
of the NAS of Ukraine*  
Kyiv, Ukraine  
starostenko.o.m@nas.gov.ua

Olga Grigoryeva  
*Institute of Macromolecular Chemistry  
of the NAS of Ukraine*  
Kyiv, Ukraine  
grigoryevaolga@i.ua

Laurent Michely  
*Institut de Chimie  
et des Matériaux Paris-Est*  
Thiais, France  
laurent.michely@cnrs.fr

Alexander Fainleib  
*Institute of Macromolecular Chemistry  
of the NAS of Ukraine*  
Kyiv, Ukraine  
fainleib@i.ua

Daniel Grande  
*Institut de Chimie  
et des Matériaux Paris-Est*  
Thiais, France  
daniel.grande@cnrs.fr

**Abstract**— The polycyclotrimerization reaction of dicyanate ester of bisphenol E (DCBE) in the presence of two different nanofillers, reactive aminopropylisobutyl POSS (APIB-POSS) or inert fullerite C<sub>60</sub> (0.1 wt.%) and thermal behavior of the nanocomposites synthesized have been investigated using differential scanning calorimetry (DSC) technique. It is noteworthy that the introduction of reactive amino-functionalized APIB-POSS into DCBE monomer accelerates dramatically the thermal curing process leading to the formation of a polycyanurate network (PCN) with chemically incorporated POSS nanoparticles. On the contrary, adding fullerite C<sub>60</sub> to DCBE decelerates polycyclotrimerization of the latter, at that increasing glass transition temperature of the PCN/C<sub>60</sub> nanocomposite was obtained.

**Keywords**—cyanate ester resin, amino-functionalized POSS, fullerite C<sub>60</sub>

## I. INTRODUCTION

Polycyanurates (PCN) from cyanate ester resins represent a family of high-performance polymers and exhibit high thermal stability (> 400°C), high glass transition temperature (> 270°C), high fire-, radiation and chemical resistance, low water absorption and low outgassing, high adhesion to different substrates and excellent dielectric properties [1]. Due to these attractive features, PCN are very promising as highly effective adhesives, sealants, and polymer matrices for composite materials. However, the high reaction temperature of the synthesis of PCN limits their application. Also, like most thermosets their main drawback is brittleness. To overcome this limitation the different approaches for modification of PCN have been developed over the past decades and are still of great interest. PCN are modified by many different additives, such as thermoplastics, elastomers, reactive oligomers with the formation of semi-IPNs, IPNs and hybrid polymer networks [1, 2]. POSS represent cage structures with the formula (RSiO<sub>1.5</sub>)<sub>n</sub>, where  $n = 8, 10, 12$  and R is hydrogen, reactive, or non-reactive organic groups. Each silicon atom is bonded to three oxygen atoms in a cage and a single R substituent out of the cage (Table I). These substituents improve the compatibility of POSS molecules

with polymers or monomers. In the case of reactive R, 3-D POSS molecules with diameters of 1-3 nm graft chemically to the polymer structure. New hybrid organic-inorganic CER-based thermosets with hydroxyl- [3, 4], amino- [5, 6] or epoxy- [7, 8] functionalized POSS units have been obtained and studied. When the CER/functionalized POSS nanocomposites exhibit the systems with nanoparticles covalently bonded to the polymer matrix, their thermal and mechanical properties are improved.

Fullerite crystals are formed of hollow spherical molecules of carbon C<sub>nc</sub>, i.e., fullerenes of varying molecular mass. It is known that compounds of crystalline structure (fullerites) break down into individual molecules (fullerenes) in a liquid phase [9].

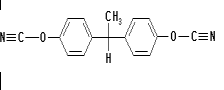
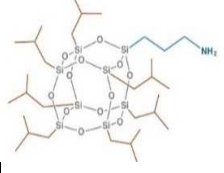
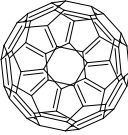
Fullerenes and their derivatives have many remarkable chemical, electronic and optical properties but to date, only a few of these properties can be exploited [10]. One reason is that C<sub>60</sub> and the other fullerenes are not easily processed. The molecules of fullerenes have a tendency to aggregate rather than remain as separate molecules. Moreover, fullerenes often consist of a mixture of regioisomers, which are difficult to separate. An alternative approach, which avoids some of these problems is to incorporate fullerenes into polymers. Incorporating and dispersing fullerenes in polymers generally enhances the processability of these extraordinary molecules and improve some specific physical properties of polymer materials, thus facilitating their application in a wide variety of areas. The combination of unique properties of fullerene with functional polymers has led to remarkable mechanical, thermal, electrical, optical, and photovoltaic properties of the final materials.

The aim of this work was to compare the curing kinetics of cyanate ester resin (CER) with the formation of a PCN network in the presence of two different inorganic nanofillers with cage structure: one of them was reactive towards CER matrix (APIB-POSS) and another one (fullerite C<sub>60</sub>) was inert, and to study the thermal behavior of the nanocomposites synthesized.

## II. EXPERIMENTAL

In the present study, the kinetic peculiarities of 1,1'-bis(4-cyanatophenyl) ethane (dicyanate ester of bisphenol E (DCBE), trademark PRIMASET® LECy, Lonza, Switzerland) polycyclotrimerization in the presence of a different type of nanofillers were investigated by DSC. The nanosized reactive organically functionalized POSS, aminopropylisobutyl POSS (APIB-POSS, Hybrid Plastics Inc., Hattiesburg, MS, USA) and inert fullerite  $C_{60}$  (Institute for Problems of Materials Science of the National Academy of Sciences of Ukraine) of 0.1 wt.% content were used as nanofillers. The crystals of the fullerite  $C_{60}$  consist of fullerene units with the number of carbon atoms per molecule equal to 60 (20 hexagons and 12 pentagons, which form a truncated icosahedron) [9]. The chemical structures and basic physical characteristics for the components used are given in Table I.

TABLE I. CHEMICAL STRUCTURE AND PHYSICAL CHARACTERISTICS OF THE COMPONENTS USED

Name	Chemical Structure	Physical Characteristics
Dicyanate ester of bisphenol E, DCBE		$M = 264 \text{ g}\cdot\text{mol}^{-1}$ $T_m = 29^\circ\text{C}$ $\rho_{20^\circ\text{C}} = 1.18 \text{ g}\cdot\text{cm}^{-3}$ $\eta = 75 \text{ mPa}\cdot\text{s}$
Aminopropylisobutyl POSS, APIB-POSS		$M = 875 \text{ g}\cdot\text{mol}^{-1}$ $\rho_{20^\circ\text{C}} = 1.16 \text{ g}\cdot\text{cm}^{-3}$ $d = 1 - 3 \text{ nm}$
Fullerene $C_{60}$		$M = 720 \text{ g}\cdot\text{mol}^{-1}$ $\rho_{20^\circ\text{C}} = 1.65 \text{ g}\cdot\text{cm}^{-3}$ $d = 0.714 \text{ nm}$

The nanofiller, i.e. APIB-POSS or fullerite  $C_{60}$ , was added to the liquid dicyanate monomer (~200 mg) and thoroughly grinded in an agate mortar for ~10 min at the ambient temperature until a transparent, i.e. homogenous, mixture. Note, the crystalline fullerite  $C_{60}$  transformed to the amorphous fullerene  $C_{60}$  during the solution procedure. Then the resulting mixture (~25-30 mg) was placed in a hermetic aluminum pan for dynamic curing during DSC measurements.

The kinetic investigations were performed using DSC 25 Differential Scanning Calorimeter in a nitrogen atmosphere by heating from 25 to 350°C at a rate of 5°C/min and the temperature position of the exothermic peaks ( $T_p$ ), reaction enthalpy ( $\Delta H_f$ ), the time of induction period onset ( $\tau_i$ , at the conversion of cyanate groups equal to 0.1 %), end time of reaction ( $\tau_{\text{end}}$ ), the maximal rate of reaction ( $W_{\text{max}}$ ), the time of maximal rate of reaction ( $\tau_{\text{max}}$ ), and total reaction time ( $\tau_{\text{tot}}$ ) were determined and analyzed. It is worth noting that the calculation of the heat of reaction for the blends was based on the net weight of the DCBE in the blends. For estimating glass transition temperatures ( $T_g$ ) of the neat PCN synthesized from DCBE, and PCN-based nanocomposites, the second DSC scans with the heating rate of 20°C/min over the temperature range from 50°C to 350°C in a nitrogen atmosphere were performed.

## III. RESULTS AND DISCUSSIONS

Fig. 1 exhibits the nonisothermal DSC exothermic curves of the curing process of the neat DCBE and the DCBE/nanofiller compositions studied with different types of nanofillers used, and their main thermal characteristics are summarized in Table II. One can clearly see that for all samples the reaction starts at  $T > 150^\circ\text{C}$ , the curves have extremal character (go through a maximum at  $T = 243\text{--}275^\circ\text{C}$ ) and the reaction finishes completely at  $T > 300^\circ\text{C}$ . For the neat DCBE sample, the exothermic maximum correlates with a peak curing temperature ( $T_p$ ), the  $T_p$  value is equal to ~260°C. There is also some weak shoulder at ~195°C that may be attributed to the formation of the intermediate DCBE dimers, trimers and, potentially, other higher even-mers [1].

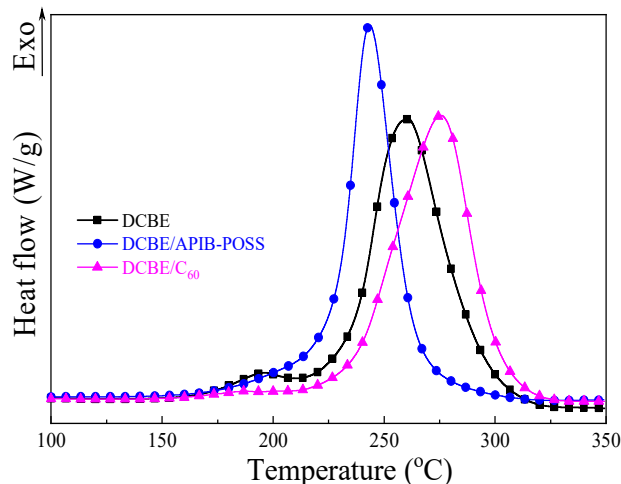


Fig. 1. DSC curves of the curing process for the neat DCBE and DCBE/nanofiller compositions.

The enthalpy of the cure reaction ( $\Delta H_f$ ) (the area under the exothermic DSC peak) for the neat DCBE was calculated to be  $\Delta H_f \sim 842 \text{ J/g}$  and it decreased significantly for both the DCBE/nanofiller compositions studied, as shown in Table II, even at such small nanofiller content (0.1 wt.%). These facts indicate the effect of the selected nanofillers on the polycyclotrimerization of the DCBE in the compositions studied, which is explained below.

The DCBE/APIB-POSS sample displays a unimodal curing profile with a distinct exothermic peak corresponding to the DCBE curing process. For the DCBE/APIB-POSS specimen the corresponding  $T_p$  value is shifted toward a much lower temperature, viz. from  $T_p \sim 261^\circ\text{C}$  (for pure DCBE) to  $T_p \sim 243^\circ\text{C}$  (Table II), additionally, a significant decrease in the value of reaction enthalpy to  $\Delta H_f \sim 691 \text{ J/g}$  was recorded for the sample. These facts evidence that the polycyclotrimerization of DCBE in the presence of amino-POSS nanoparticles mostly is occurred at lower temperatures due to the catalytic effect of the reactive nanofiller. The catalytic effect of the amino-POSS is also confirmed by the temperature dependences of the conversion of cyanate group ( $-\text{O}-\text{C}\equiv\text{N}$ ) of DCBE (Fig. 2) and the reaction time dependences of the reaction rate of polycyclotrimerization of DCBE (Fig. 3) calculated from the DSC data. From Fig. 2 and 3, it is also clearly seen that polycyclotrimerization of the DCBE matrix is characterized by a certain induction period

TABLE II. KINETIC PARAMETERS OF DCBE POLYMERIZATION IN THE ABSENCE AND THE PRESENCE OF 0.1 WT.% OF NANOFILLER

Sample	$T_p, ^\circ\text{C}$	$\Delta H_f, \text{J/g}$	$\tau_i/\tau_{\text{end}}, \text{min}$	$W_{\text{max}}, \%/ \text{min}$	$\tau_{\text{max}}, \text{min}$	$\tau_{\text{tot}}, \text{min}$
DCBE	261	842	23/61	10.9	47	38
DCBE /APIB-POSS	243	691	20/56	17.0	43	36
DCBE /C <sub>60</sub>	275	786	26/60	11.5	50	34

( $\tau_i$ ) for the DCBE/APIB-POSS sample (Figs. 1-3) which is 3 min shorter than that of the pure DCBE sample (Table II).

In addition, the maximal rate of reaction,  $W_{\text{max}}$ , increases by 6.1 %/min with the introduction of APIB-POSS to DCBE and the time to the maximal rate of reaction,  $\tau_{\text{max}}$ , decreased by 4 min for DCBE/APIB-POSS composition (Table II). Therefore, the introduction of APIB-POSS into the DCBE reaction medium significantly accelerated the conversion of  $-\text{O}-\text{C}\equiv\text{N}$  groups from the early stages of PCN network formation, also the total time of reaction is 2 min shorter than that of the pure DCBE sample. We suppose that the catalytic effect of amino-functionalized POSS on DCBE polymerization is explained by the well-known reaction of amino groups of different modifiers with cyanate group with the formation of isourea intermediate fragments, which are good catalysts for cyanates polycyclotrimerization [1, 11, 12] (Fig. 4).

In its turn an introduction of fullerite C<sub>60</sub> as an inert nanofiller into the DCBE resin has a significant inhibitory effect on the process of polycyclotrimerization of DCBE: the induction period  $\tau_i \approx 26$  min (Table II) is longer compared to both the neat DCBE and DCBE/APIB-POSS compositions; also the position of the  $T_p$  peak shifts to a higher temperature ( $T_p \sim 275^\circ\text{C}$ ) that is by  $14^\circ\text{C}$  higher in comparison to the neat

pure DCBE network ( $T_p \sim 261^\circ\text{C}$ ) (Fig. 1, Table II). From the temperature dependence of cyanate groups conversion ( $\alpha$ ) (Fig. 2) and the reaction time dependences of the reaction rate of polycyclotrimerization of DCBE (Fig. 3) one can see that polycyclotrimerization of DCBE in the presence of C<sub>60</sub> go decidedly slowly than for the pure DCBE and DCBE/APIB-POSS samples. However, for DCBE/C<sub>60</sub> sample decreasing in the  $\Delta H_f$  value also was recorded. All these data evidence that although C<sub>60</sub> filler does not catalyze the polymerization of DCBE due to its chemical inertness towards cyanates, nevertheless it affects the curing process.

It was found that all the cured PCN-based nanocomposites investigated possessed high  $T_g$  values, which vary from  $273^\circ\text{C}$  to  $281^\circ\text{C}$  depending on the composition (Fig. 5). Chemical grafting of APIB-POSS nanoparticles into PCN provides a slightly higher  $T_g$  value compared to that for individual PCN (Table III). On one side embedding of cage particles have to limit the relaxation of PCN polymer chains leading to increasing  $T_g$  value, on the other side the appearance of linear fragments containing isourea linkages must facilitate the relaxation behavior of PCN lowering  $T_g$ . Probably, the resulting effect of the competition of these two processes determines the close values of  $T_g$  for these two systems studied.

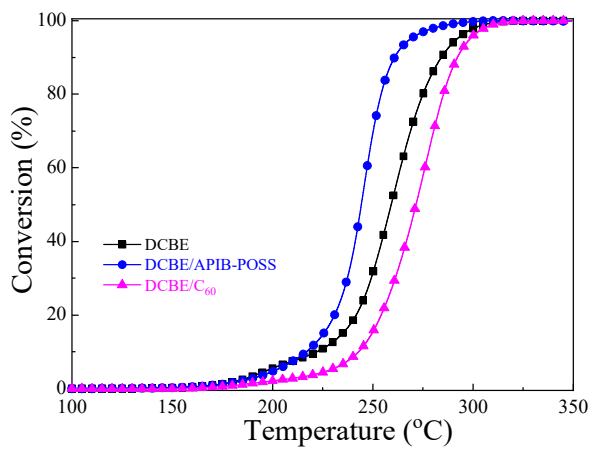
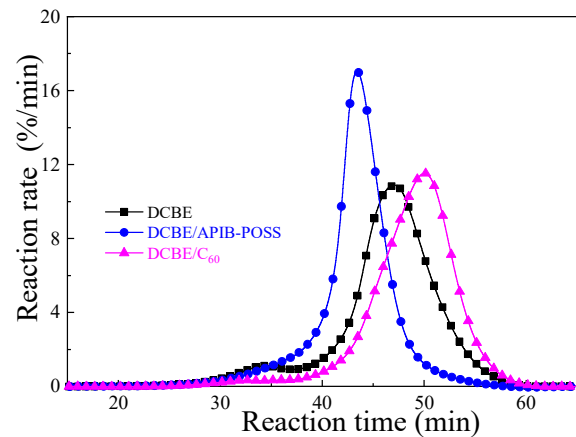
Fig. 2. Temperature dependence of  $-\text{OCN}$  groups conversion.

Fig. 3. Reaction rate curves of curing process for the neat DCBE and DCBE/nanofiller compositions.

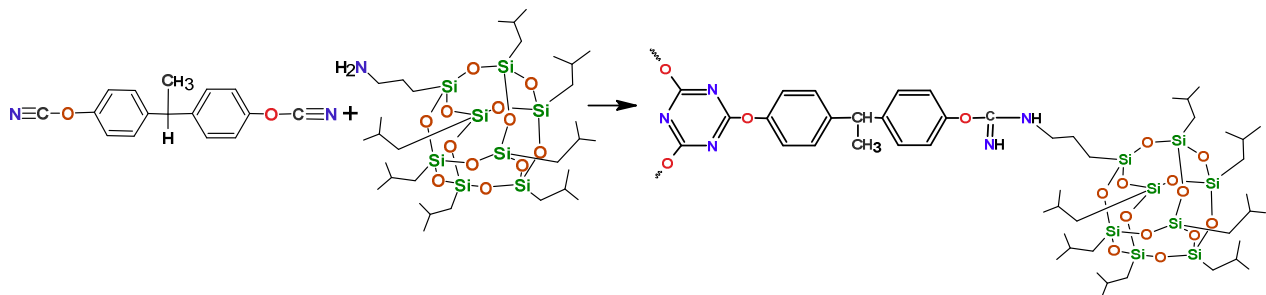


Fig. 4. Schematic presentation of the chemical incorporation of APIB-POSS particles into the growing PCN network.

The PCN/C<sub>60</sub> composite exhibits a high  $T_g$ , which is higher by  $\sim 7.6$  °C compared to the  $T_g$  value of the neat PCN. One can suppose that small C<sub>60</sub> molecules ( $d = 0.714$  nm) inert towards cyanate groups of growing PCN network do not chemically incorporate into the PCN network structure and just are placed in a free volume of PCN network (Fig. 6). Thus, in this case, there is no formation of any fragments that facilitate the relaxation of the PCN, but filling their free volume with C<sub>60</sub> particles (that play the role of additional reinforce cage for the network) can obviously slow down the relaxation of the PCN, providing an increase in the  $T_g$  value. This conclusion is confirmed by a significant decrease in the  $\Delta C_p$  values for both synthesized nanocomposites compared to the pure PCN sample (Table III).

TABLE III. THERMAL CHARACTERISTICS (DSC DATA) OF THE NEAT DCBE AND PCN/NANOFILLER NANOCOMPOSITES

Sample	$T_g$ , °C	$T_{g(\text{onset})}/T_{g(\text{end})}$ , °C/°C	$\Delta C_p$ , J/g
PCN	273.6	265/283	0.333
PCN / APIB-POSS	274.2	265/282	0.258
PCN / C <sub>60</sub>	281.2	271/289	0.234

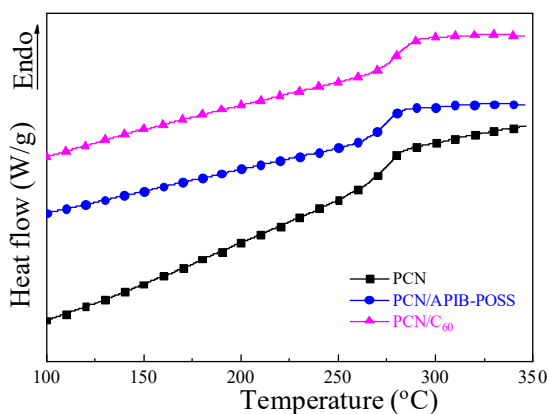


Fig. 5. DSC thermograms (2<sup>nd</sup> scan) for the neat PCN and PCN/nanofiller nanocomposites created.

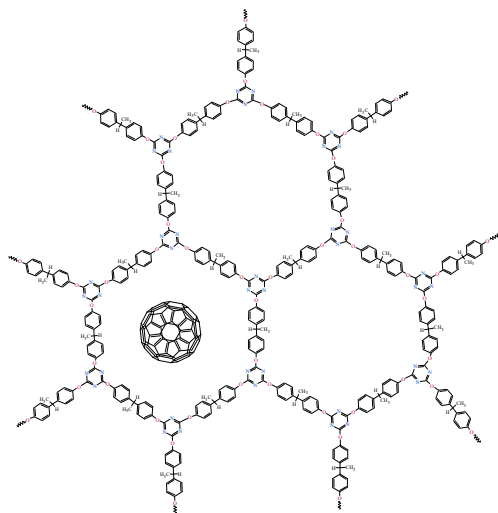


Fig. 6. Schematic presentation of incorporation of fullerene C<sub>60</sub> in PCN network.

#### IV. CONCLUSIONS

The studies carried out in this work have shown that the high-temperature polycyclotrimerization of DCBE is catalyzed by even 0.1 wt.% of reactive amino-functionalized POSS, which ensures the polymerization of DCBE at lower temperatures and in a narrower time interval; the PCN/APIB-POSS nanocomposite synthesized also has a higher  $T_g$  value. In turn, the 0.1 wt.% of inert C<sub>60</sub> fullerene slows down the polymerization of DCBE but increases the  $T_g$  value of the resulting PCN/C<sub>60</sub> nanocomposite. It has been established that using small amounts of the APIB-POSS or C<sub>60</sub> in the synthesis of heat-resistant PCN-based nanocomposites does not lead to the defectiveness of the PCN matrix formed, and provides an improvement in thermal behavior of PCN/APIB-POSS and PCN/C<sub>60</sub> nanocomposites studied.

#### ACKNOWLEDGMENT

NASU and CNRS are gratefully acknowledged for financial support through French-Ukrainian International Associated Laboratory on Nanoporous Thermostable Polymer Materials “LIA POLYNANOPOR” and POLYTHERMAT International Research Project.

#### REFERENCES

- [1] I. Hamerton, *Chemistry and Technology of Cyanate Ester Resins*. Chapman & Hall, Glasgow, 1994.
- [2] A. Fainleib, *Thermostable Polycyanurates. Synthesis, Modification, Structure and Properties*. New York: Nova Science Publisher, 2010.
- [3] Y. Lin, J. Jin, M. Song, S. Shaw, and C. Stone, “Curing dynamics and network formation of cyanate ester resin/polyhedral oligomeric silsesquioxane nanocomposites,” *Polymer*, vol. 52, 2011, pp. 1716–1724.
- [4] K. Liang, G. Li, H. Toghiani, J. Koo, and C. Pittman, “Cyanate ester/polyhedral oligomeric silsesquioxane (POSS) Nanocomposites: Synthesis and Characterization,” *Chem. Mater.*, vol. 18, pp.301–312, 2006.
- [5] Z. Zhang, G. Liang, X. Wang, S. Adhikari, and J. Pei, “Curing behavior and dielectric properties of amino-functionalized polyhedral oligomeric silsesquioxane/cyanate ester resin hybrids,” *High Performance Polymers*, pp.1–9, 2013.
- [6] H. Cho, K. Liang, and S. Chatterjee, “Synthesis, morphology, and viscoelastic properties of polyhedral oligomeric silsesquioxane nanocomposites with epoxy and cyanate ester matrices,” *J. Inorg. Organomet. Polym.*, vol. 15, pp.541–553, 2005.
- [7] V. Bershtein, A. Fainleib, P. Yakushev, D. Kirilenko, L. Egorova, O. Grigoryeva, V. Ryzhov, and O. Starostenko, “High performance multi-functional cyanate ester oligomer-based network and epoxy-POSS containing nanocomposites: Structure, dynamics, and properties,” *Polym. Compos.*, vol. 41, pp.1900–1912, 2020.
- [8] Z. Zhang, G. Liang, and X. Wang, “Epoxy-functionalized polyhedral oligomeric silsesquioxane/cyanate ester resin organic-inorganic hybrids with enhanced mechanical and thermal properties,” *Polym. Int.*, vol. 63, 2014, pp. 552–559.
- [9] P. Eklund and A. Rao, *Fullerene Polymers and Fullerene Polymer Composites*. New-York: Springer, 2002.
- [10] P. Harris, “Fullerene polymers: a brief review,” *C.*, vol. 6, p.71, 2020.
- [11] E. Grigat and R. Pütter, “Chemie der cyansäureester, iv. umsetzung von cyansäureestern mit amino- bzw. iminogruppenhaltigen substanzen,” *Chem. Ber.*, vol. 97, pp. 3027–3035, 1964.
- [12] V. Bershtein, A. Fainleib, L. Egorova, K. Gusakova, O. Grigoryeva, D. Kirilenko, S. Konnikov, V. Ryzhov, P. Yakushev, and N. Lavrenyuk, “The impact of ultra-low amounts of amino-modified MMT on dynamics and properties of densely cross-linked cyanate ester resins,” *Nanoscale Res. Lett.*, vol.10, p.165, 2015.