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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-03938814>

Submitted on 3 Feb 2023

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

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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 C₆₀ (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 C₆₀ to DCBE decelerates polycyclotrimerization of the latter, at that increasing glass transition temperature of the PCN/C₆₀ nanocomposite was obtained.

Keywords—cyanate ester resin, amino-functionalized POSS, fullerite C₆₀

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_{1.5})_n, 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_{nc}, 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].

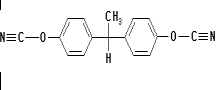
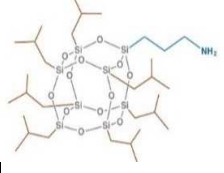
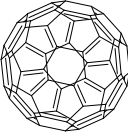
Fullerenes and their derivatives have many remarkable chemical, electronic and optical properties but to date, only a few of these properties can be exploited [10]. One reason is that C₆₀ and the other fullerenes are not easily processed. The molecules of fullerenes have a tendency to aggregate rather 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 C₆₀) 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 C₆₀ (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 C₆₀ 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 C₆₀, 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 C₆₀ transformed to the amorphous fullerene C₆₀ 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 (ΔH_f), the time of induction period onset (τ_i , at the conversion of cyanate groups equal to 0.1 %), end time of reaction (τ_{end}), the maximal rate of reaction (W_{max}), the time of maximal rate of reaction (τ_{max}), and total reaction time (τ_{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].

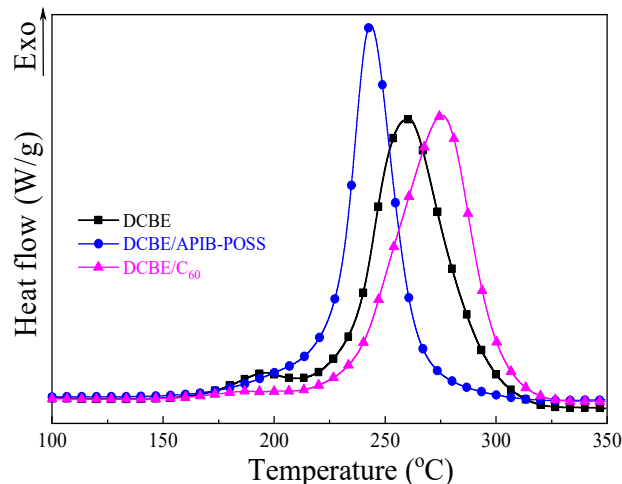


Fig. 1. DSC curves of the curing process for the neat DCBE and DCBE/nanofiller compositions.

The enthalpy of the cure reaction (ΔH_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 ₆₀ | 275 | 786 | 26/60 | 11.5 | 50 | 34 |

(τ_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_{max} , increases by 6.1 %/min with the introduction of APIB-POSS to DCBE and the time to the maximal rate of reaction, τ_{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 C₆₀ 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°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 (α) (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 C₆₀ go decidedly slowly than for the pure DCBE and DCBE/APIB-POSS samples. However, for DCBE/C₆₀ sample decreasing in the ΔH_f value also was recorded. All these data evidence that although C₆₀ 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°C to 281°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.

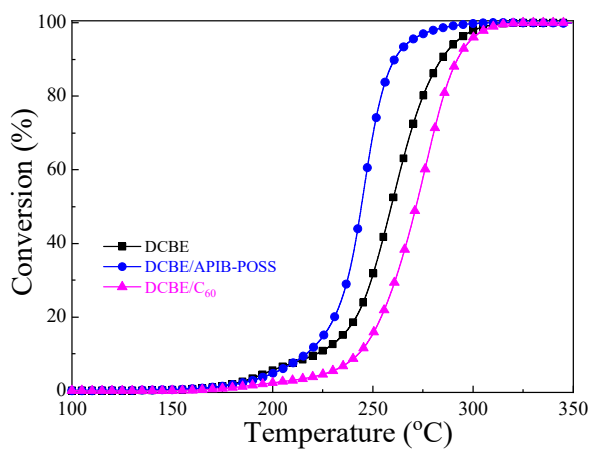
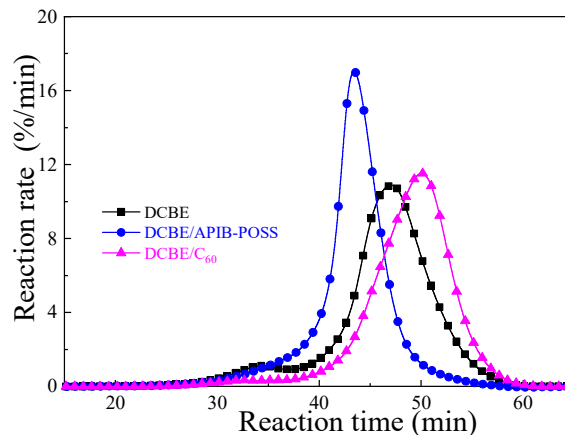
Fig. 2. Temperature dependence of $-\text{OCN}$ groups conversion.

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

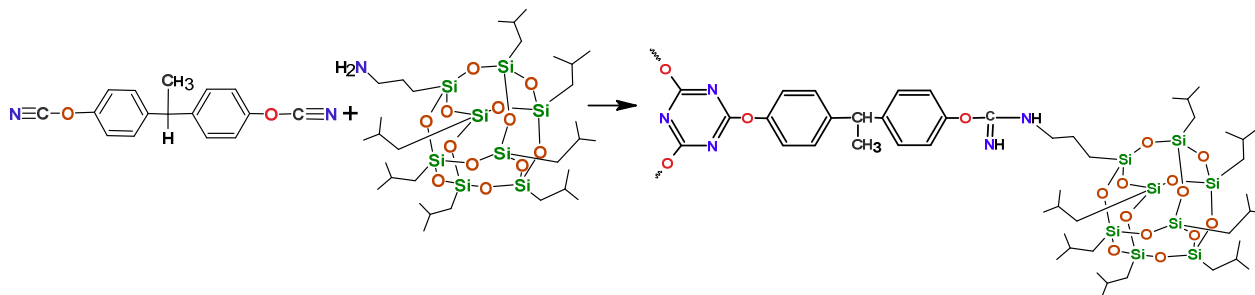


Fig. 4. Schematic presentation of the chemical incorporation of APIB-POSS particles into the growing PCN network.

The PCN/C₆₀ composite exhibits a high T_g , which is higher by ~ 7.6 °C compared to the T_g value of the neat PCN. One can suppose that small C₆₀ 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 C₆₀ 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 ΔC_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 | ΔC_p , J/g |
|-----------------------|------------|-------------------------------------------------|--------------------|
| PCN | 273.6 | 265/283 | 0.333 |
| PCN / APIB-POSS | 274.2 | 265/282 | 0.258 |
| PCN / C ₆₀ | 281.2 | 271/289 | 0.234 |

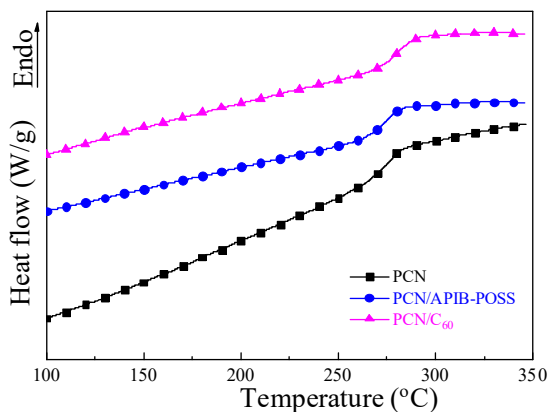


Fig. 5. DSC thermograms (2nd scan) for the neat PCN and PCN/nanofiller nanocomposites created.

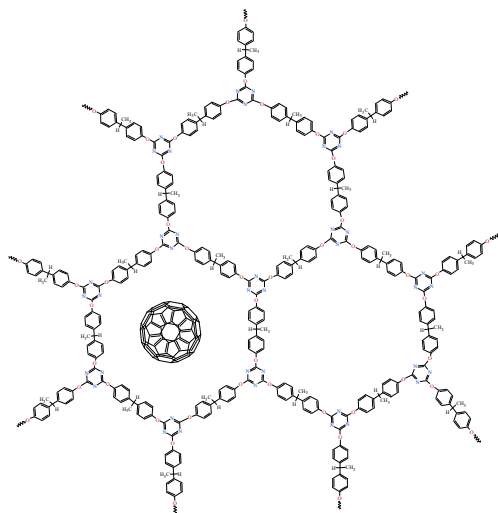


Fig. 6. Schematic presentation of incorporation of fullerene C₆₀ in PCN network.

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 C₆₀ fullerene slows down the polymerization of DCBE but increases the T_g value of the resulting PCN/C₆₀ nanocomposite. It has been established that using small amounts of the APIB-POSS or C₆₀ 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/C₆₀ 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.

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