ОГЛЯД

REVIEW

https://doi.org/10.15407/polymerj.44.02.093
UDC 547.874.1

A.M. FAINLEIB,
Institute of Macromolecular Chemistry of the National Academy of Sciences of Ukraine, 48, Kharkivske shose, Kyiv, 02160, Ukraine,
e-mail: fainleib@i.ua
ORCID: 0000-0001-8658-4219

BIO-BASED CYANATE ESTER RESINS AND THERMOSTABLE POLYMER NETWORKS DERIVED THEREOF. MINI REVIEW.

This article is devoted to a review of the literature on a very promising direction in the chemistry of macromolecular compounds: the synthesis and study of polymers, more specifically, high performance polycyanurates based on bis(poly) phenols) of natural origin. Cyanate Ester Resins (CER) are characterized by a very regular structure of the polymer networks, namely polycyanurates (PCNs), obtained by their polycyclotrimerization. They have received much attention because of their unique combination of physical properties, including 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 (ε=2,64–3,11). As a result, CER are currently used as structural or functional materials in aeronautics, space (composite strakes, fins, nose radomes, heat shields), printed circuit boards, adhesives etc. It has to be noted here that CER thermosetting resins, expanding the high-temperature operations regimes, are produced from synthetic petroleum-derived bisphenols, such as bisphenol A, which are toxic and dangerous for environment. In the past decade, naturally occurring phenolic derivatives have arisen as attractive precursors for developing new materials from renewable bio-sources for use in eco-friendly processes. Resins have been prepared utilizing either the whole liquid product or a phenolic-enriched fraction obtained after fractional condensation or further processing, such as solvent extraction or use of greener extraction methods. However, to date, none of the phenolic production and fractionation techniques has been utilized to allow for substitution of 100% of the phenol content of the resin without impacting its effectiveness compared to commercial formulations based on petroleum-derived phenol. The variable nature of the percentage of phenolic compounds in terms of purity from different batches of crops from one season to another and geographical influence does not allow from the reproducibility of phenolic compounds, and hence the resulting polymers. However, the direction that needs to be explored should be oriented towards complete replacement of petro-based phenolics with bio-based ones in the face of an urgent petroleum crisis. In addition, there is a necessity for materials showing enhanced applicability and improved performance. It is a beginning of the era of such a step, which requires further exploration of natural phenolic sources aimed at their enhanced utilization.

Key words: *natural phenolic compounds, bio-based cyanate ester resins, thermostable polymer networks, polycyanurates.*

Thermosetting polymer matrices are widely used in aerospace industry and microelectronics. Among them, Cyanate Ester Resins (CER) expand the high-temperature operation regime, thus constituting the most promising materials.

CER-based crosslinked polymers possess high glass transition temperature and high thermal stability. The chemistry of CER curing reaction is given in Fig. 1.

CER differ from others by a very regular structure of the polymer networks, namely polycyanurates (PCNs), obtained by their polycyclotrimerization [1-5]. They have received much attention because of their unique combination of physical properties, including high thermal stability

Цитування: Fainleib A.M. Bio-based cyanate ester resins and thermostable polymer networks derived thereof. Mini review. *Полімерний журнал*. 2022. **44**, № 2. С. 93—100. https://doi.org/10.15407/polymerj.44.02.093

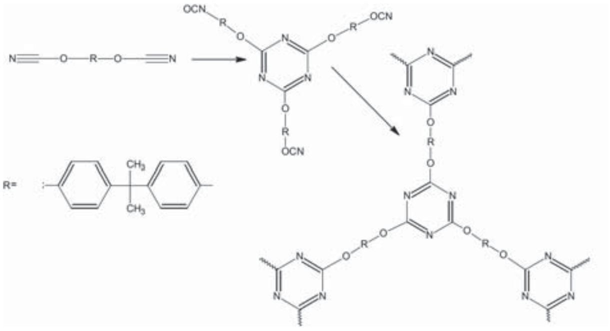

Fig. 1. Polycyclotrimerization of cyanate ester resins to polycyanurate networks

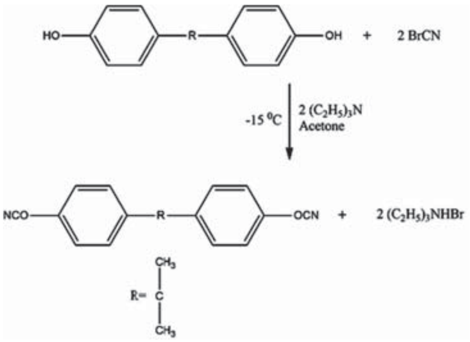

Fig. 2. Synthesis of cyanate ester resin, namely dicyanate ester of bisphenol A

(> 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 (ε = 2.64–3.11) [2–4]. As a result, CER are currently used as structural or functional materials in aeronautics, space (composite strakes, fins, nose radomes, heat shields), printed circuit boards, adhesives etc. [6]. The following companies manufacture CER for these applications: Cytec Aerospace Materials, Hexcel, Huntsman Advanced Materials, JFC Technologies, Lonza, Henkel, TenCate Advanced Composites. However, like for most thermosets the main drawback of polymer networks obtained from CER is brittleness. To overcome this limitation, for example, modification of CER has been developed over the past decades and is still of great interest. CER are modified by many different additives, such as engineering thermoplastics, elastomers, reactive oligomers [2–9] with formation of semi-IPNs, IPNs and hybrid networks. These effects are reached due to the microphase-separated morphology generation (co-continuous phases of the components).

It has to be noted here that CER thermosetting resins, expanding the high-temperature operations regimes, are produced from synthetic petroleum-derived bisphenols, such as bisphenol A (see Fig. 2), which are toxic and dangerous for environment.

There is a diverse group of naturally occurring compounds containing multiple phenolic functionalities. These compounds are commonly found in higher plants. Importantly, they are commercially available, have synthetic, medicinal, and industrial value. Over the last decade, chemists have made significant efforts to replace the latter bisphenols by biomass-based products and produce thermosetting resins thereof [10-14]. Recently a few reports on synthesis and characterization of CERs from natural phenols and their further transformation to thermally stable polymers have appeared [15–21].

In our opinion, this group has a high potential as a source of the raw materials for synthesis of CER. This will allow developing a number of biodegradable high performance thermosets of varying structure and properties. For example, the derivatives of *Proanthocyanidin, Galloyl and hexahydroxydiphenyl Ester, Hydroxy cinnamic acid, Phloroglucinol* etc. can be used as a natural source for producing the aforementioned resins and their thermosets of specific structure and properties for high temperature operations. The other rich source of polyphenols (more than 160 polyphenols) is *Salvia*, an important genus widely cultivated and used in flavoring and folk medicines. Thus, *Caffeic acid metabolites*, *Phenolic glycosides, Flavonoids* can also be considered as a promising raw material for producing CERs their polymer networks (polycyanurates). First successful attempts of synthesis of CERs from natural polyphenols have been recently reported.

Recently, strategies to prepare CERs from fully or partly regenerable raw materials have been proposed. Meylemans et al. [15, 16] from Research Department, Chemistry Division, U.S. Navy and Air Force Research Laboratory, Aerospace Systems Directorate ultimately used lignin as a polymeric raw material basis that is accessible from the wood-based industry; it represents a natural polyphenolic resin of varying constitution and composition. Lignin has been tested since a long time as

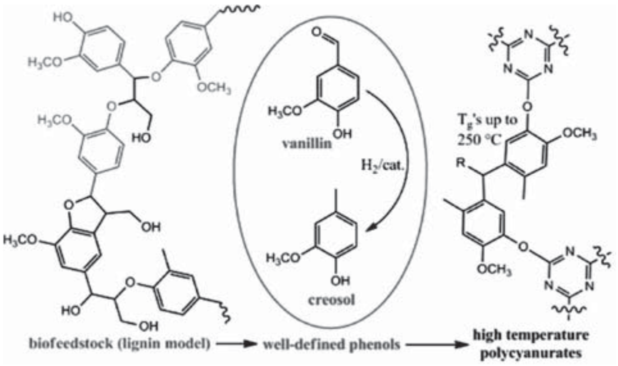

Fig. 3. Conversion of lignin to well-defined phenolics and high performance polycyanurates [15]

a natural-based substitute for phenolic monomers or oligomers in phenolic resins and numerous other polymers. Hence, it seems reasonable to investigate this versatile raw material as a source for monomers applicable in CER production. Authors suggest producing well-defined phenolics, such as vanillin and, in turn, creosol, from conversion of lignin and, by dimerization, further transforming these into bisphenols, which are then suitable as precursors for cyanate ester resin production.

A series of renewable dicyanate esters have been prepared from bisphenols synthesized by condensation of 2-methoxy-4-methylphenol (creosol) with formaldehyde, acetaldehyde, and propionaldehyde and further polymerized to high performance polycyanurates (Fig. 3, 4) [15].

The cyanate esters have been fully characterized by infrared spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and single crystal X-ray diffraction [15]. These compounds melt from 88 to 143 °C, while cured resins have glass transition temperatures from 219 to 248 °C, water uptake (96 h, 85 °C immersion) in the range of 2.05–3.21 %, and wet glass transition temperatures from 174 to 193 °C. These properties suggest that creosol-derived cyanate esters may be useful for a wide variety of military and commercial applications. The cure chemistry of the cyanate esters has been studied with FTIR spectroscopy and differential scanning calorimetry. The results show that cyanate esters with more sterically demanding bridging groups cure more slowly, but also more completely than those with a bridging methylene group. In addition to

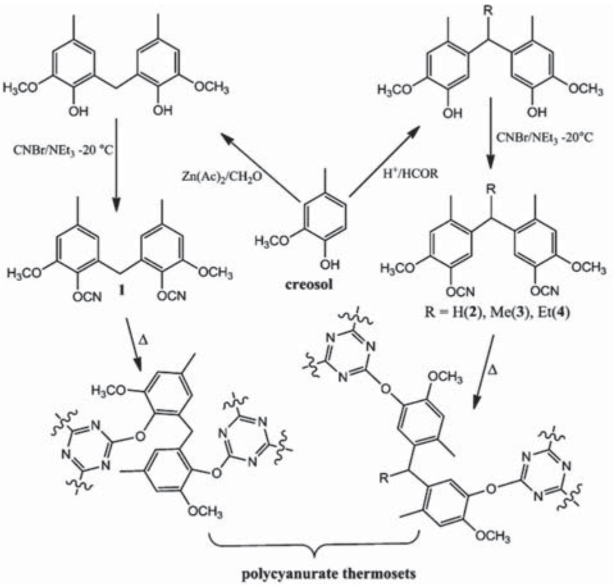

Fig. 4. Synthesis of Bis(cyanate) Esters and Polycyanurate Thermosets from Creosol

the structural differences, the purity of the cyanate esters has a significant effect on both the cure chemistry and final T_g of the materials. In some cases, post-cure of the resins at 350 °C resulted in significant decomposition and off-gassing, but cure protocols that terminated at 250–300 °C generated void-free resin pucks without degradation. Thermogravimetric analysis revealed [15] that the cured resins were stable up to 400 °C and then rapidly degraded. TGA/FTIR and mass spectrometry results showed that the resins decomposed to phenols, isocyanic acid, and secondary decomposition products, including CO_2. Char yields of the cured resins under N_2 ranged from 27 to 35 %, while char yields in air ranged from 8 to 11 % [15].

These data suggest that resins of this type may potentially be recycled to parent phenols, creosol, and other alkylated creosols by pyrolysis in the presence of excess water vapor. The ability to synthesize these high temperature resins from a phenol (creosol) that can be derived from lignin, coupled with the potential to recycle the composites, provides a possible route to the production of sustainable, high-performance, thermosetting resins with reduced environmental impact.

Renewable phenols derived from biomass sources often contain methoxy groups that alter the properties of derivative polymers. To evaluate the impact of o-methoxy groups on the performance characteristics of cyanate ester resins,

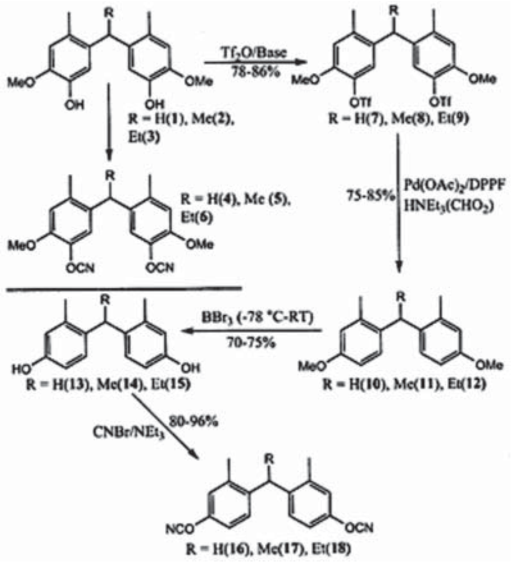

Fig. 5. Synthesis of deoxygenated CER from renewable bisphenols [38]

three bisphenols derived from the renewable phenol creosol were deoxygenated by conversion to ditriflates followed by palladium-catalyzed elimination and hydrolysis of the methoxy groups. The deoxygenated bisphenols were then converted to the following cyanate ester resins: bis(4-cyanato-2-methylphenyl)methane (16), 4,4′-(ethane-1,1′-diyl)bis(1-cyanato-3-methylbenzene) (17), and 4,4′-(propane-1,1′-diyl)bis-(1-cyanato-3-methylbenzene) (18) (Fig. 5) and cured to the corresponding polycyanurate networks [17].

The physical properties, cure chemistry, and thermal stability of these resins were evaluated and compared to those of cyanate esters derived from the oxygenated bisphenols [17]. 16 and 18 had melting points 37 and > 95 °C lower, respectively, than the oxygenated versions, while 17 had a melting point 14 °C higher. The $T_{g's}$ of thermosets generated from the deoxygenated resins ranged from 267 to 283 °C, up to 30 °C higher than the oxygenated resins, while the onset of thermal degradation was 50–80 °C higher. The deoxygenated resins also exhibited water uptakes up to 43 % lower and wet $T_{g's}$ up to 37 °C higher than the oxygenated resins. TGA-FTIR of thermoset networks derived from 16–18 revealed a different decomposition mechanism compared to the oxygenated resins. Instead of a low-temperature pathway that resulted in the evolution of phenolic compounds, 16–18 had significantly higher char yields and decomposed via evolution of small molecules including isocyanic acid, CH_4, CO_2, and NH_3.

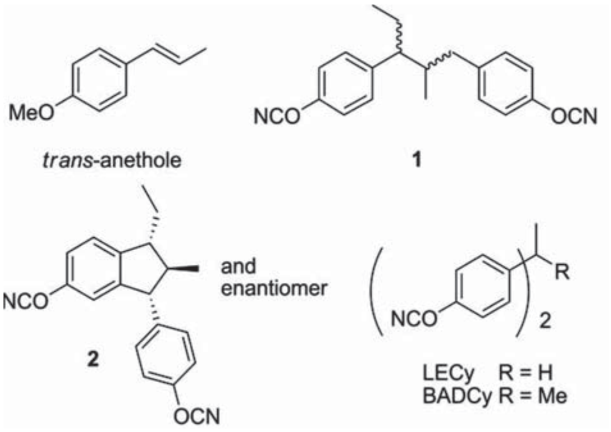

Fig. 6. Chemical structures of dicyanates (1, 2) derived from trans-anethole and two commercial dicyanate esters LECy and BADCy [18]

Davis *et al.* demonstrated that trans-anethole can be chemically transformed into suitable precursor molecules for the preparation of CER (Fig. 6) that show a technological performance comparable to currently available commercial resins [18].

This approach is highly interesting since it exploits re-generable plant oil as an alternative resource for phenolic compounds. Trans-anethole is the major ingredient (to about 90%) of the essential oil of star anise (*Illicium verum*) and can be obtained from the crude oil. The oil is produced in amounts of approximately 400 metric tons per annum for the preparation of flavor and fragrance products, which of course is not much compared to the petrochemical-based manufacturing of phenols or even to the amounts of lignin that are amounting as byproducts from the wood industry. However, exploiting new high-performance applications of high added value might possibly act as an incentive to increase the crop production and hence improve availability in the long term [18]. Especially the properties of the CER obtained from RRR/SSS 1-ethyl-2-methyl-3-(4-cyanatophenyl)-5-cyanatoindane displayed a remarkably high glass transition temperature of 313 °C, which was superior to the LECy-based commercial reference CER; further, it had a lower water uptake (1.66 %) than for the two LECy and BADCy reference cyanate esters. The glass transition temperature measured after 96 h immersion in water at 85 °C was still 223 °C, which was somewhat lower than for the commercial reference materials, but still within an acceptable range. The CER obtained

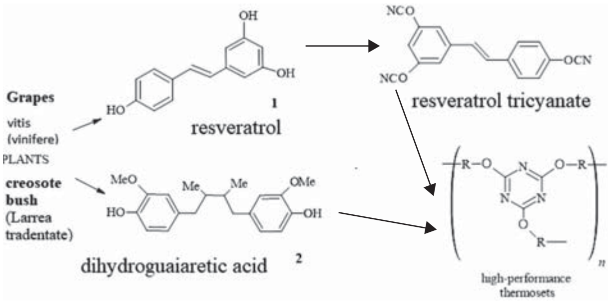

Fig. 7. Synthesis of polycyanurate network from resveratrol (1) and dihydroguaiaretic acid (2)

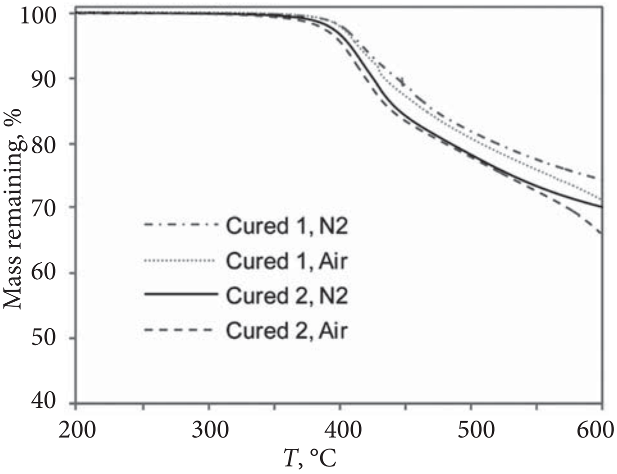

Fig. 8. TGA traces of cured products 1 and 2

from the other monomer, racemic 1,3-bis(4-cyanatophenyl)-2-methylpentane, displayed comparatively inferior properties.

The tricyanate esters of the natural products resveratrol (1) and dihydroresveratrol (2) isolated from grapes (*Vitim vinifera*) and creosote bush (*Larrea tridentate*), respectively, were synthesized and subjected to thermal curing, which gave polycyanurate networks (Fig. 7) exhibited glass transition temperatures of > 340 °C and 334 °C for the cured 1 and cured 2, respectively [19, 20].

Thermal decomposition temperatures of 412 °C and 403 °C for the polycyanurates 1 and 2, respectively, were typical of this class. However, char yields (600 °C) of 71 % and 66 % for 1 and 2, respectively, were surprisingly more than double that from the commercial polycyanurate of bisphenol A dicyanate (25 %). It is especially strange to get such high values of char yields in air (see Fig. 8).

Among the renewable resource materials, cashew nut shell liquid (CNSL) is considered as an important starting material due to its unique structural features, abundant availability and low cost. A large number of chemicals and products have been developed starting from CNSL by taking advantage of the three reactive sites, namely, phenolic hydroxyl, aromatic ring and unsaturation(s) in the alkenyl side chain [21]. Polymers derived from CNSL have certain outstanding properties, which make them unique for many applications [22–24]. The derived polymers exhibit flexibility due to “internal plasticization” resulting from the presence of a long side-chain, which also imparts hydrophobic character to the materials. CNSL has low fade characteristics, which makes it a desirable component in brake lining formulations. CNSL has inherent anti-microbial and anti-termite properties.

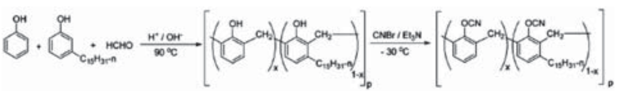

Fig. 9. Synthesis of cardanol-based CER

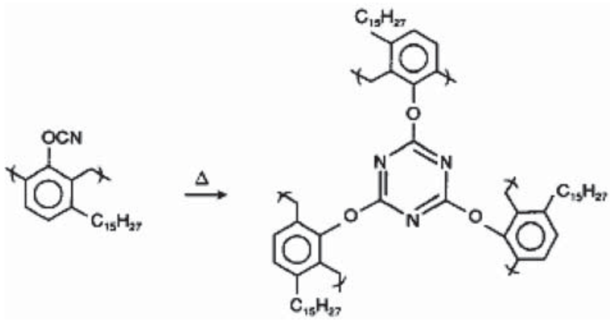

Fig. 10. Synthesis of cardanol-based polycyanurate

Cardanol incorporated-phenol–formaldehyde novolac resins can be transformed to their corresponding cyanate esters, which on thermal curing provide thermally stable phenolic-triazine networks. Nair *et al.* [25] studied the synthesis of cardanol modified-phenol–formaldehyde novolac resins by acid and base catalyzed reactions and the corresponding cyanate esters (Fig. 9).

In Fig. 10 polycyclotrimerization of the cardanol-based CER is schematically presented. The authors have also studied thermal cure characteristics and related energy aspects of the cyanate esters, which depended on the composition. The presence of cardanol proportionately facilitated the curing. The thermal characterization of the novolac and the corresponding cured phenolic-triazine networks (polycyanurates) indicated a

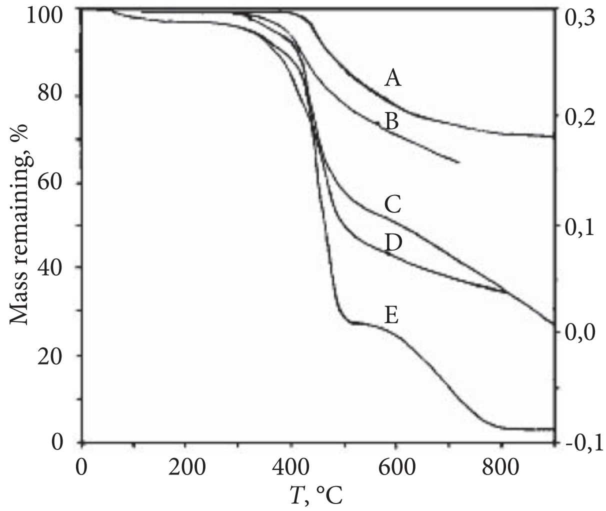

Fig. 11. Thermograms of polycyanurate from CER based on the blends of pure novolac resin (*A*) and cardanol (see Fig. 9) with cardanol content: 0 (*A*), 20 (*B*), 40 (*C*), 50 (*D*), 100 % (*E*) in N_2 (heating rate 20 °C/min) [25]

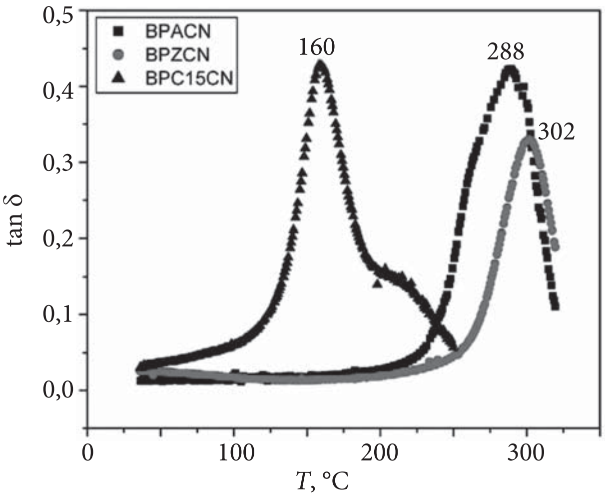

Fig. 12. Tan δ versus temperature dependence for polycyanurates based on 2,2-bis(4-cyanatophenyl) propane (BPACN), 1,1-bis(4-cyanatophenyl)cyclohexane (BPZCN), 1,1-bis(4-cyanatophenyl) 3-pentadecyl cyclohexane (BPC15CN) [26]

detrimental effect of cardanol on the thermal stability and char residue of the resins (Fig. 11).

The cardanol based cyanate ester monomer, *viz.*, 1,1-bis(4-cyanatophenyl)3-pentadecylcyclohexane (BPC15CN) was synthesized and cured by employing a copper acetylacetonate–nonylphenol catalyst system [26]. This cardanol based cyanate ester resin showed better processability coupled with lower melting points, lower cure onset with broad cure exotherm than commercial cyanate ester resin based on bisphenol A. The cured BPC15CN showed good thermal stability ($T_{d10\%}$ = 413 °C). A depression in T_g (T_g = 160 °C) was observed (Fig. 12), which could be attributed to the presence of a flexible pentadecyl chain, which also helps in lowering the moisture absorption.

Therefore, the global ground-breaking aim of this work is to analyze the perspectives of a replacement of the synthetic petroleum-based polyphenolic raw materials currently used in synthesis of high-performance polymers and their composites for specific applications like aerospace structures and microelectronics by the selected commercially available non-toxic biomass-derived biodegradable polyphenols to alleviate the wide-spread dependence on fossil fuels and, enhance environment, security, and economy. As follows from the analysis of current state of the art, few papers were published on synthesis and characterization of CERs from natural polyphenols and their further transformation into thermally stable polymers.

In the past decade, naturally occurring phenolic derivatives have arisen as attractive precursors for developing new materials from renewable biosources for use in eco-friendly processes. Resins have been prepared utilizing either the whole liquid product or a phenolic-enriched fraction obtained after fractional condensation or further processing, such as solvent extraction or use of greener extraction methods. However, to date, none of the phenolic production and fractionation techniques has been utilized to allow for substitution of 100% of the phenol content of the resin without impacting its effectiveness compared to commercial formulations based on petroleum-derived phenol. The variable nature of the percentage of phenolic compounds in terms of purity from different batches of crops from one season to another and geographical influence does not allow from the reproducibility of phenolic compounds, and hence the resulting polymers. However, the direction that needs to be explored should be oriented towards complete replacement of petro-based phenolics with bio-based ones in the face of an urgent petroleum crisis. In addition, there is a necessity for materials showing enhanced applicability and improved performance. It is a beginning of the era of such a step, which requires further exploration of natural phenolic sources aimed at their enhanced utilization.

To our knowledge, there were no publications either on organic-inorganic hybrid nanocomposites based on above-mentioned high-performance resins derived from natural polyphenols as well as on commercialization of the latter for producing adhesives, coatings, encapsulants, carbon or glass plastics, as well as membranes.

REFERENCES

1. *Shimp D.A., Christenson J.R., Ising S.J.* In book: Proceedings of the 34th Annual International SAMPE Symposium, 1989: 222–223.
2. Chemistry and technology of cyanate ester resins / Ed Ian Hamerton. London: Chapman & Hall, 1994: 357. ISBN: 0-7514-0044-0.
3. *Hamerton I., Hay J.N.* Recent technological developments in cyanate ester resins. High Performance Polymers, 1998, **10**, no. 2: 163–174. https://doi.org/10.1088/0954-0083/10/2/001.
4. *Nair C.P.R., Mathew D., Ninan K.N.* Cyanate Ester Resins, Recent Developments. Advances in Polymer Science, 2001, **155**, 1–99.
5. Thermostable polycyanurates. Synthesis, modification, structure and properties / Ed Alexander Fainleib. New York: Nova Science Publisher, 2010: 362. ISBN: 978-1-60876-907-0.
6. *McConnell V.P.* Resins for the Hot Zone, Part II: BMIs, CEs, benzoxazines and phthalonitriles. High Performance Composites, 2009, **17**, no. 9: 49–54.
7. *Fainleib A.M., Shantalii T.A., Pankratov V.A.* Copolymers of cyanate esters and plastics based on them. Kompozitsionnye Polimernye Materialy, 1991, **49**: 39–53.
8. *Fainleib A.M., Sergeeva L.M., Shantalii T.A.* Triazine-containing interpenetrating polymer networks. Kompozitsionnye Polimernye Materialy, 1991, **50**: 63–72.
9. *Fainleib A., Grigoryeva O., Pissis P.* Modification of polycyanurates by polyethers, polyesters and polyurethanes. Hybrid and interpenetrating polymer networks, Chapter 3. In book: Focus on natural and synthetic polymer science / Ed Cornelia Vasile and G.E. Zaikov. New York: Nova Science Publishers, 2006, 49–84. ISBN: 1-60021-115-1.
10. *Handique J.G., Baruah J.B.* Polyphenolic compounds: an overview. Reactive & Functional Polymers, 2002, **52**, no. 3: 163–188. https://doi.org/10.1016/S1381-5148(02)00091-3.
11. *Yinrong Lu, L. Yeap Foo.* Polyphenolics of Salvia—a review. Phytochemistry, 2002, **59**, 117– 140. https://doi.org/10.1016/S0031-9422(01)00415-0.
12. *Ronda J.C, Lligadas G., Galià M., Cádiz V.* A renewable approach to thermosetting resins. Reactive & Functional Polymers, 2013, **73**, no. 2: 381–395. https://doi.org/10.1016/j.reactfunctpolym.2012.03.015.
13. *Bobade S.K., Paluvai N.R., Mohanty S., Nayak S.K.* Bio-Based Thermosetting Resins for Future Generation: A Review, Polymer-Plastics Technology and Engineering, 2016, **55**, no. 17: 1863–1896. https://doi.org/10.1080/03602559.2016.1185624.
14. *Espinosa L.M.*, *Meier M.A.R.* Plant oils: The perfect renewable resource for polymer science?! European Polymer Journal, 2011, **47**, no. 5: 837–852. https://doi.org/10.1016/j.eurpolymj.2010.11.020.
15. *Meylemans H.A., Harvey B.G., Reams G.T., Guenthner A.J., Cambrea L.R., Groshens T.J., Baldwin L.C., Garrison M.D., Mabry J.M.* Synthesis, Characterization, and Cure Chemistry of Renewable Bis(cyanate) Esters Derived from 2-Methoxy-4-Methylphenol Biomacromolecules, 2013, **14**: 771–780. https://doi.org/10.1021/bm3018438.
16. *Meylemans, H.A., Groshens, T.J., Harvey, B.G.* Synthesis of renewable bisphenols from creosol. ChemSusChem, 2011, **5**, no. 1: 206–210. https://doi.org/10.1002/cssc.201100402.
17. *Harvey B.G., Guenthner A.J., Lai W.W., Meylemans H.A., Davis M.C., Cambrea L.R., Reams G.T., Lamison K.R.* Effects of o-Methoxy Groups on the Properties and Thermal Stability of Renewable High-Temperature Cyanate Ester Resins. Macromolecules, 2015, **48**, 3173–3179. https://doi.org/ 10.1021/acs.macromol.5b00496.
18. *Davis M.C., Guenthner A.J., Groshens T.J., Reams J.T., Mabry J.M.* Polycyanurate Networks from Anethole Dimers: Synthesis and Characterization. Journal of Polymer Science, Part A: Polymer Chemistry, 2012, 50, 4127–4136. https://doi.org/10.1002/pola.26218.
19. *Cash J.J., Davis M.C., Ford M.D., Groshens T.J., Guenthner A.J., Harvey B.G., Lamison K.R., Mabry J.M., Meylemans H.A., Reams J.T., Sahagun C.M.* High Tg thermosetting resins from resveratrol. Polymer Chemistry, 2013, **4**: 3859–3865. https://doi.org/10.1039/c3py00438d.
20. Pat. 8853343 USA. IC^7 C08G 63/02. Thermoset compositions from plant polyphenols. M.C. Davis, A.J. Guenthner, J.J. Cash, Publ. 07.10.2014.
21. *Voirin C., Caillol S., Sadavarte N.V., Tawade B.V., Boutevin B., Wadgaonkar P.P.* Functionalization of cardanol: towards biobased polymers and additives. Polymer Chemistry, 2014, **5**: 3142–3162. https://doi.org/10.1039/C3PY01194A.

22. *Balachandran V.S., Jadhav S.R., Vemula P.K., John G.* Recent advances in cardanol chemistry in a nutshell: from a nut to nanomaterials. Chemical Society Reviews, 2013, **42**, no. 2: 427–438. https://doi.org/10.1039/C2CS35344J.
23. *Mele G., Vasapollo G., Del Sole R.* Cardanol-Based Materials as Natural Precursors for Olefin Metathesis. Molecules, 2011, **16**, no. 8: 6871–6882. https://doi.org/10.3390/molecules16086871.
24. *Caillol S.* Cardanol: A promising building block for biobased polymers and additives. Current opinion in green and sustainable chemistry, Elsevier, 2018, **14**: 26–32. https://doi.org/10.1016/j.cogsc.2018.05.002.
25. *Nair C.P.R., Bindu R.L., Joseph V.C.* Journal of Polymer Science, Part A: Polymer Chemistry, 1995, **33**: 621–627. https://doi.org/10.1002/pola.1995.080330403.
26. *Arun D. Kulkarni, Bhausaheb V. Tawade and Prakash P. Wadgaonkar.* Cyanate ester resins containing pentadecyl-substituted cyclohexyl moiety: Synthesis, curing and structure–property relationship. High Performance Polymers, 2012, **25**, no. 3: 278–286. https://doi.org/10.1177/0954008312463738.

Received 03.05.2022

О.М. Файнлейб,
Інститут хімії високомолекулярних сполук Національної академії наук України, 48, Харківське шосе, Київ 02160, Україна
e-mail: fainleib@i.ua

ЦІАНАТНО-ЕСТЕРНІ СМОЛИ НА НАТУРАЛЬНІЙ ОСНОВІ ТА ЇХ ТЕРМОСТАБІЛЬНІ ПОЛІМЕРНІ СІТКИ. МІНІ ОГЛЯД

Ця стаття присвячена огляду літератури щодо перспективного напряму у хімії високомолекулярних сполук: синтезу та дослідженню високотехнологічних термостійких поліціануратів на основі біс(полі)фенолів природного походження. Ціанатно-естерні смоли (ЦЕС) характеризуються високо регулярною структурою полімерних сіток, а саме поліціануратів (ПЦ), отриманих шляхом поліциклотримеризації ЦЕС. Цим матеріалам приділяється велика увага через унікальну комбінацію фізико-хімічних властивостей, включаючи високу термічну стабільність (> 400 °C), високу температуру склування (> 270 °C), високі вогне-, радіаційну та хімічну стійкість, низькі водопоглинання та газовиділення, високу адгезію до різних матеріалів, низькі діелектричні втрати (ε=2,64–3,11) тощо. Натепер термореактивні ЦЕС використовуються як конструкційні або функціональні матеріали в аеронавтиці, космосі (для виготовлення фюзеляжів, крил, хвостового оперення, деталей інтер’єру, носових обтічників, теплозахисних екранів літаків і ракет тощо), друковані плати, клеї тощо. Слід зазначити, що застосування термореактивних смол ЦЕС істотно розширює високотемпературні діапазони роботи отриманих на їх основі матеріалів і конструкційних деталей, однак ці смоли виробляються з синтетичних нафтових бісфенолів, таких як бісфенол А, які досить токсичні та небезпечні для навколишнього середовища. Тому останнім часом фенольні сполуки природного походження привернули увагу дослідників і промисловців як привабливі прекурсори для розробки нових матеріалів з відновлюваних біо-джерел для використання в екологічно безпечних процесах. Фенольні смоли рослинного походження готують з використанням або цілого рідкого продукту, або збагаченої фенолом фракції, отриманої після фракційної конденсації чи подальшої обробки, наприклад, екстракції розчинником або використання більш екологічно чистих методів екстракції. Однак на сьогодні жоден із методів виробництва та фракціонування фенолів не був використаний для заміни 100 %-вого вмісту фенолу в смолі без впливу на її ефективність порівняно з комерційними рецептурами на основі фенолу, отриманого з нафти. Змінний характер відсоткового вмісту фенольних сполук за чистотою від різних партій посівів від одного сезону до іншого та географічний вплив не дають змоги відтворювати фенольні сполуки, а отже, й отримані полімери. Однак напрям, який необхідно досліджувати, має бути орієнтований на повну заміну фенольних сполук на основі нафти на біо-продукти за умов невідкладної нафтової кризи. Крім того, існує необхідність у матеріалах з покращеними характеристиками. Це початок нової ери, що вимагає подальшого вивчення природних фенольних джерел з метою їх більш широкого використання.

Ключові слова: фенольні сполуки природного походження, ціанатно-естерні смоли на натуральній основі, термостабільні полімерні сітки, поліціанурати.