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## COPOLYMERS AND INTERPENETRATING POLYMER NETWORKS OF THERMOREACTIVE NITROGEN-CONTAINING RESINS. MINI REVIEW

*In a short review the effective methods of optimization of structure and properties of high-performance polymers obtained from thermoreactive nitrogen-containing resins such as benzoxazines, bismaleimides, cyanate esters have been analysed. High crosslinked density copolymer thermosets are synthesized through chemical interactions between reactive functional groups, which belong to the monomers/oligomers used. The different possible processes such as copolymerization or formation of interpenetrating polymer networks are discussed. The high-performance polymers and composites from thermoreactive nitrogen-containing resins are effectively used in aerospace industry and microelectronics as materials possessing high thermal and thermooxidative stability, radiation and chemical resistance, low water absorption, low dielectric loss, high dimension stability and high adhesion to different substrate. The performance characteristics of this kind of materials can be controlled by changing their composition, temperature-time curing schedule, using catalytic systems.*

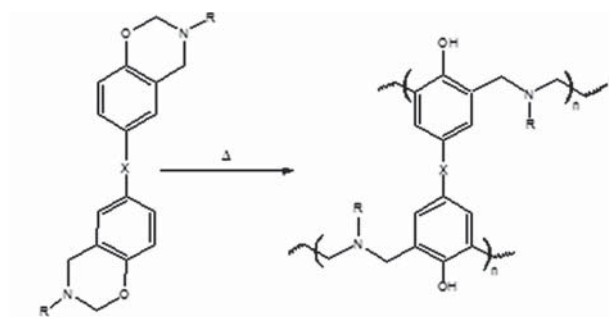
**Keywords:** copolymers, IPNs, thermoreactive resins, benzoxazine, bismaleimide, cyanate ester resins.

Modern high-tech industries, such as aerospace and microelectronics, place high demands on the polymer materials and composites to be used. Such materials must withstand high loads at elevated temperatures, high humidity, and radiation. Just a few high-performance nitrogen-containing resins of the materials on the market, meet high requirements. Bismaleimides, benzoxazines, cyanate ester resins and bisphthalonitriles exhibit high thermal and thermooxidative stability, moisture, radiation and chemical resistance. While carbon and glass fiber reinforced composites, adhesives, coatings and casting compounds based on traditional epoxy resins provide high mechanical characteristics usually at temperatures up to 150 °C, the above-mentioned nitrogen-containing thermosetting polymers are operable at 250 °C,

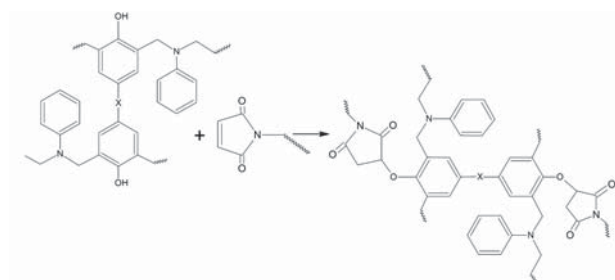
and some of them at 300 °C and higher. Each of these polymers has its own advantages and disadvantages, and scientists and engineers working in this field try to find ways to optimize the synthesis methods, structure and properties of these materials. One of the directions is to obtain copolymers of these polymers. Due to the high chemical activity, the functional groups of such monomers/oligomers easily enter into chemical interaction with the formation of densely cross-linked copolymers that contain mixed nitrogen-containing heterocycles in their structure, providing an optimal combination of the necessary characteristics for the efficient operation of these materials.

Thermostable polymer matrices are widely used in aerospace industry and microelectronics. Among them, thermosetting Benzoxazines

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Scheme 1. Polymerization of benzoxazines



Scheme 2. Copolymerization of benzoxazines with bismaleimides

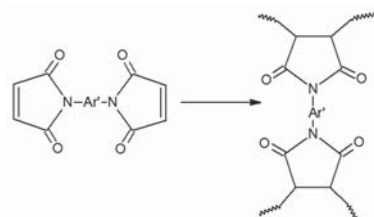
(BOAs), Bismaleimides (BMIs), Cyanate Ester Resins (CERs) and Bisphthalonitriles (BPhNs) expand the high-temperature operation regime, thus constituting the most promising materials.

It is well known that the benzoxazine ring is stable at low temperature, but a ring opening reaction occurs at high temperature, and novolac type oligomers having both phenolic hydroxyl group and tertiary amine group are produced (Scheme 1) [1, 2].

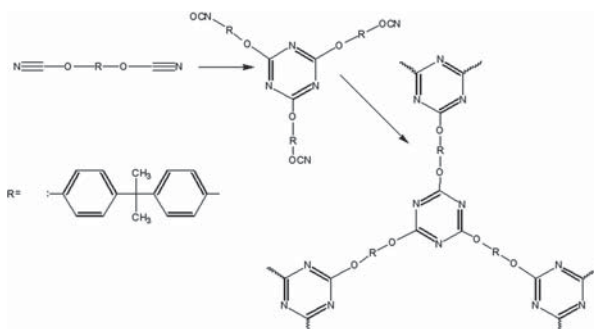
Using this benzoxazine compound as a phenolic resin, it is expected to develop a new type of phenolic resin that releases no volatiles during curing reaction and needs no catalysts. Benzoxazine monomers exhibit many other attractive properties, such as low melt viscosity. In addition, the polymer is characterized by low volumetric shrinkage upon polymerization, low moisture absorption, excellent chemical resistance, flame retardancy, electrical properties, thermal stability and mechanical properties; and very rich molecular design flexibility [2]. For high temperature operations, BOAs have to be cured. Recently, maleimide-modified (Scheme 2) and furan-modified benzoxazines have been synthesized, and the properties of the cured resins have been investigated [2-7]. Nanocomposites using benzoxazines also have been reported [8-12].

BMI- and CER-based crosslinked polymers possess high glass transition temperature and high thermal stability. The chemistry of BMI and CER curing reactions are given in Scheme 3 and 4, correspondingly.

At the same time, these polymers are very brittle, and their processing as such to fabricate articles is strongly complicated by high curing temperatures and limited durability. To overcome these problems, it is of common practice to use reactive diluents (reactive co-monomers) to improve resin processability. Consequently, the ideal co-monomer would function both as a reactive diluent, *i.e.* liquid at room temperature, and as toughening agent. The key issue to use a co-monomer is that the co-monomer undergoes a linear chain extension reaction with the BMI to reduce the crosslinking density in the fully cured resin. For example, 2,2'-diallylbisphenol-A (DABPA) is used as a co-monomer capable of reacting via the Michael reaction with BMI. The technological properties of the system based on 4,4'-(*N,N'*-bismaleimide) diphenylmethane (BMDPM) and DABPA turned to be excellent, but the different reactions involved are quite complex, *i.e.* -ene and -diene addition reaction, Michael reaction, Diels-Alder reaction, homopolymerization, copolymerization, reverse Diels-Alder reaction, etc. [13]. The brittleness was



Scheme 3. Polymerization of bismaleimides



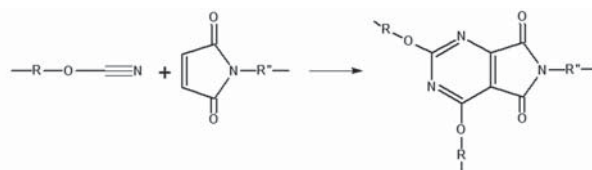
Scheme 4. Polyclotrimers of dicyanates into cyanate ester resins

also substantially reduced, with retaining the high heat resistance. Recent works on BMDPM/DAB-PA have shown that it was possible to crosslink the system by electron-beam (EB) or by UV at room temperature [14].

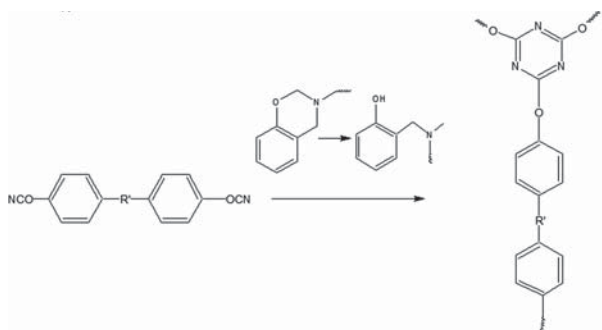
CERs differ from others by a very regular structure of the polymer networks, namely polycyanurates (PCNs), obtained by their polycyclo-trimerization [15-19]. They have received much attention because of their unique combination of physical properties, including high thermal stability (> 400 °C), high 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 ( $\epsilon = 2.64\text{--}3.11$ ) [16-18]. As a result, CERs are currently used as structural or functional materials in aeronautics, space (composite strakes, fins, nose radomes, heat shields), printed circuit boards, adhesives etc. [20].

The following companies manufacture CER for these applications: Cytec Aerospace Materials, Hexcel, Huntsman Advanced Materials, JFC Technologies, Lonza, Henkel, TenCate Advanced Composites. By the way, some of these companies also produce BOAs (Huntsman, Henkel) and BMIs (Cytec, Hexcel, TenCate). However, like for most thermosets their main drawback is brittleness. To overcome this limitation modification of CERs has been developed over the past decade and is still of great interest. CERs are modified by many different additives, such as engineering thermoplastics, elastomers, reactive oligomers [16-19, 21-27] with formation of semi-IPNs, IPNs and hybrid networks. As thermoplastics with high glass transition temperature, polysulphones, polyethersulphones, polyimides, polyetherimides, polyarylates, and polycarbonates can be used [28-42]. 5-fold increases in GIC fracture toughness, 2-fold increases in tensile strength, and 5-fold increases in tensile elongation-at-break, 2.5-fold in unnotched Izod impact strength are characteristic of these thermoplastic-modified CER networks (semi-IPNs) [28]. These effects are reached due to the microphase-separated morphology generation (co-continuous phases of the components). The peak of these publications falls on the late 90s and early 2000s.

Unfortunately, the improvement of mechanical properties is generally reached at the expense of thermal stability. This deficiency is remedied by



**Scheme 5.** Copolymerization of bismaleimides with cyanate monomers

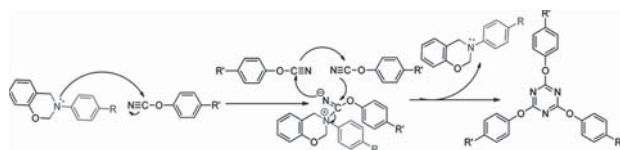


R – phenyl.

**Scheme 6.** Copolymerization of benzoxazines with cyanate ester resins according to Ref. 66–68

synthesis of nanocomposites of PCNs with montmorillonite, carbon nanotubes, nanostructured aluminium borate, ZnO,  $\text{ZrW}_2\text{O}_8$ , nanosilica, and polyhedral oligomeric silsesquioxanes (POSS) [43-61]. The most pronounced effect on mechanical and thermal properties of PCNs is achieved when nanoparticles with organically modified surface are used.

Over the last decades, several papers were published on polymer networks (or IPNs) synthesized from blends of BMI/CER and BOA/CER [62-68]. For the moment, there is no univocal understanding of the chemical structure of these materials. Fan *et al.* [62], for example, consider that in BMI/CER each monomer forms an own polymer network, which interpenetrate to each other (IPNs), and there is no co-reaction between BMI and CER. Alternatively, Wu *et al.* [63] suppose a co-reaction between cyanate groups of CER and double bonds of maleimide cycle of BMI with formation

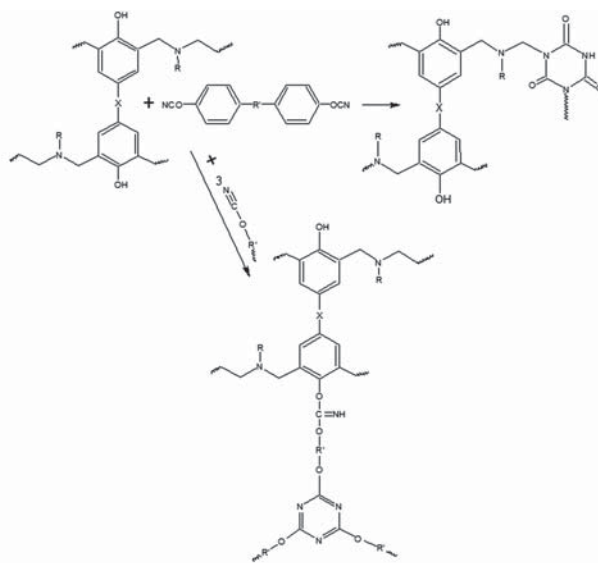


**Scheme 7.** Copolymerization of benzoxazines with cyanate ester resins according to Ref. 69

of pyrimidine-containing fragments as copolymer network junctions (**Scheme 5**).

Kimura *et al.* [66, 67] and Kumar *et al.* [68] confirmed the formation of co-networks in the BOA/CER blends (**Scheme 6**).

The authors assume that isomerization of cyanurate cycles into isocyanurate cycles occurred. The authors noted that a single  $T_g$  value of the blends implied a near homogeneous matrix [68]. The thermal stability of the blends was improved compared to polybenzoxazine matrix. By co-curing cyanate ester with polybenzoxazine, the cure reactions were facilitated and a homogeneous and high modulus polymer matrix was formed. The cured BMI/CER IPN resin systems showed [62] excellent thermal stability, which could be demonstrated by 5% weight loss temperature ( $T_{d5\%}$ ) ranging between 409 and 423 °C, maximum decomposition rate temperature ( $T_{dmax}$ ) ranging between 423 and 451 °C, and the char residue at 800 °C ranging from 37 to 41 % in nitrogen. The cured thermosetting resin from benzoxazine and cyanate ester resin had superior heat resistance, electrical resistance and water resistance to those from benzoxazine and epoxy resin [66].



**Scheme 8.** Alternative route for copolymerization of benzoxazines with cyanate ester resins

However, Wang *et al.* [69] consider that benzoxazine just catalyzes polycyclotrimerization of CER monomers and the catalytic effect results from the benzoxazine itself, not from the ring-opened structure of benzoxazine (**Scheme 7**).

In **Scheme 8**, a possible structure of the co-networks formed at a joint curing of CER/BOA blends is presented. We suppose that indeed the co-network of CER and BOA formed at thermal curing of their blends, but not IPNs because cyanate groups of CER are very reactive towards phenolic groups formed at ring-opening polymerization of benzoxazine. It was confirmed in the recent paper

**Table 1. Basic properties of high-performance thermosets**

Property	Epoxy	BMIs	CERs	BOAs
Density (g/cm <sup>3</sup> )	1,20–1,25	1,2–1,3	1,15–1,35	1,12–1,19
Curing temperature (°C)	RT–180	220–300	180–280	160–220
Curing shrinkage (%)	>3	0,007	~ 3	~ 0
Maximum continuous-use temperature (°C)	80–200	230–320	150–250	130–250
TGA onset temperature (°C)	260–340	360–400	400–420	340–370
Elongation (%)	3,0–4,3	3	2–4	2,3–2,9
Glass transition temperature	150–220	230–380	250–270	160–240
Dielectric constant (1 MHz)	3,8–4,5	3,4–3,7	2,7–3,2	3,0–3,6
Tensile modulus (GPa)	3,1–3,8	3,4–4,1	3,1–3,4	3,8–4,5
Coefficient of thermal expansion at RT (10 <sup>-6</sup> /°C)	45–65	30–50	54–71	58–69
Water uptake (%)	4–5	< 2,5	0,7–2,5	< 2



published by C Karikal Chozhan *et al.* [70]. Polybenzoxazine and cyanate ester hybrid polymer matrices were developed via solvent method. The thermal and morphological properties of benzoxazine–cyanate ester-modified hybrid systems were studied and compared with those of neat matrices. DSC results revealed that the hybrid matrices exhibited higher  $T_g$ s and curing behavior than that of neat hybrid matrices. The hybrid matrices yielded higher char yield than those of neat hybrid matrices.

The increase in the values of LOI indicates that the hybrid matrices exhibited better flame resistance than that of neat hybrid matrices [70]. Data resulted from thermal studies infer that these hy-

brid matrices can be utilized in the form of thermally stable encapsulation, adhesive, sealants, and matrices for different engineering applications.

The combination of **Scheme 5** and **8** gives imagination on possible structure of CER/BOA/BMI terpolymer obtained *via* thermal co-curing [71].

The basic performance characteristics of high-performance polymer matrices including CER-, BMI-, and BOA-based crosslinked polymers are listed in **Table 1**. The advantages and disadvantages of these thermosets are presented in **Table 2**.

Analyzing these tables and the data from different publications, we can assume that BOA components will bring to the complex systems

Table 2. Criteria for selection of polymer thermosets

Matrix type	Advantages	Disadvantages
<b>Epoxy resins</b>	<ul style="list-style-type: none"> <li>• low cost</li> <li>• commercially available</li> </ul>	<ul style="list-style-type: none"> <li>• low thermal stability</li> <li>• unacceptably poor hot/wet performance</li> </ul>
<b>BMI</b> s	<ul style="list-style-type: none"> <li>• high modulus</li> <li>• enables affordable, lightweight tooling with excellent machinability and durability</li> <li>• can be processed at the same cost as high-temperature epoxy resins</li> </ul>	<ul style="list-style-type: none"> <li>• poor processability; poor solubility in ordinary solvents</li> <li>• narrow processing window</li> <li>• relatively high dielectric constant</li> <li>• low strength</li> <li>• very low elongation at break</li> </ul>
<b>CER</b> s	<ul style="list-style-type: none"> <li>• dimensional stability at molten temperatures</li> <li>• excellent adhesion to conductor metals at <math>T \sim 250</math> °C</li> <li>• high fracture toughness with a service temperature between epoxy resins and BMIs</li> <li>• unusually low capacitance properties</li> <li>• low dissipation factor</li> <li>• low dielectric constant</li> </ul>	<ul style="list-style-type: none"> <li>• very high post-curing temperature (<math>T=250-300</math> °C) is usually required</li> </ul>
<b>BOA</b> s	<ul style="list-style-type: none"> <li>• low cost raw materials</li> <li>• low melt viscosity</li> <li>• no release of volatiles during polymerization</li> <li>• no feed for harsh catalyst or any added initiator</li> <li>• near-zero volumetric shrinkage upon polymerization</li> <li>• low tan delta</li> <li>• varying crosslink degree</li> <li>• good sound and noise absorbance</li> </ul>	<ul style="list-style-type: none"> <li>• very harmful initial raw materials (phenols, aldehydes, amines)</li> <li>• less cross-linked than other thermosets</li> </ul>

[Data from: *Thermosets: Structure, Properties, and Applications* ed. by Qipeng Guo, Elsevier, 2012; *Handbook of Thermoset Plastics* ed. by H. Dodiuk, S.H. Goodman, William Andrew, 2013; *Reactive Polymers Fundamentals and Applications: A Concise Guide to Industrial Polymers* Johannes Karl Fink, William Andrew, 2013]

higher toughness (namely storage modulus, flexural strength and flexural modulus, and lower curing temperature), BMIs will improve high temperature performance, and CERs will contribute to higher glass transition temperature, higher adhesion to different substrates, lower dielectric loss, and lower water uptake.

Finally, we have to note that in order to design

material, which meet the requirements of a specific field of application one can select some of high performance polymers described above or combine them through copolymerization process or creating interpenetrating polymer networks. The resulting structure and properties of the end product can be controlled by changing components ratio, curing schedule, using specific catalysts, fillers.

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#### КОПОЛІМЕРИ ТА ВЗАЄМОПРОНИКНІ ПОЛІМЕРНІ СІТКИ ТЕРМОРЕАКТИВНИХ АЗОТОВМІСНИХ СМОЛ. МІНІ ОГЛЯД

У короткому огляді проаналізовані ефективні методи оптимізації структури та властивостей високоефективних полімерів, отриманих з терморективних азотовмісних смол, таких як бензоксазини, бісмалеїміди, ціанові естери бісфенолів. Кополімери терморективних азотовмісних смол високої щільності зшивання синтезують завдяки хімічній взаємодії між реакційноздатними функціональними групами, які належать до мономерів/олігомерів, що використовуються. Обговорені різні можливі процеси, що мають місце при високотемпературному комбінуванні таких реактопластів, такі як кополімеризація або формування взаємопроникних полімерних сіток. Високоефективні полімери та композити з терморективних азотовмісних смол успішно використовуються в аерокосмічній промисловості та мікроелектроніці як матеріали, що володіють високою термо- і термоокиснювальною стабільністю, радіаційною і хімічною стійкістю, низьким водо/волого поглинанням, низькими діелектричними втратами, високою стабільністю розмірів і високою адгезією до різних субстратів. Експлуатаційні характеристики цього виду матеріалів можна контролювати, змінюючи їх склад, режим температурно-часового отверднення, використовуючи специфічні каталітичні системи та наповнювачі.

**Ключові слова:** кополімери, ВПС, терморективні смоли, бензоксазин, бісмалеїмід, ціанові естери бісфенолів.