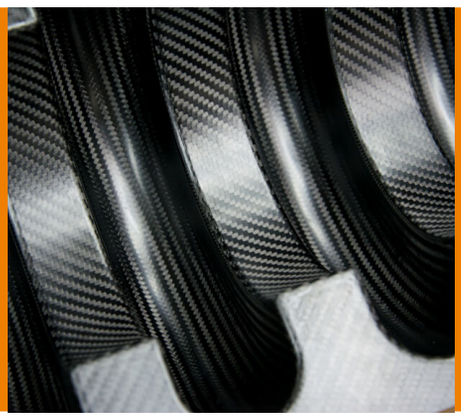
SPECIFIC POLYMERS

Tel : +33 (0)4 99 74 91 35
Fax : +33 (0)4 99 74 91 52

contact@specificpolymers.fr
www.specificpolymers.fr



05 High Performance Thermosets

Introduction

These last years have witnessed an increasing need in aerospace and automotive industries for high performance resins that can combine simultaneously the lightweight of organic materials with the high thermal resistance of metallic materials. These resins are the bismaleimides, polyimides, cyanates ester, benzoxazines and phthalonitriles.

Such polymers have been particularly attractive in the composites' area for structural and hot section components requiring higher service temperatures resistance than classic composites, prepared so far from polyamide, epoxy, vinyl ester, phenolic, polypropylene or unsaturated polyester. As a matter of fact, a 7 % per year growth of the high-performance resin market is expected in the five forthcoming years, only considering the field of aeronautic.

Even though these resins have already proved themselves in several aeronautic applications, improvements are still required. The ability of these resins to withstand high temperature for very long time without get degraded while containing the product cost is still a key challenge.

A large panel of high-performance resins

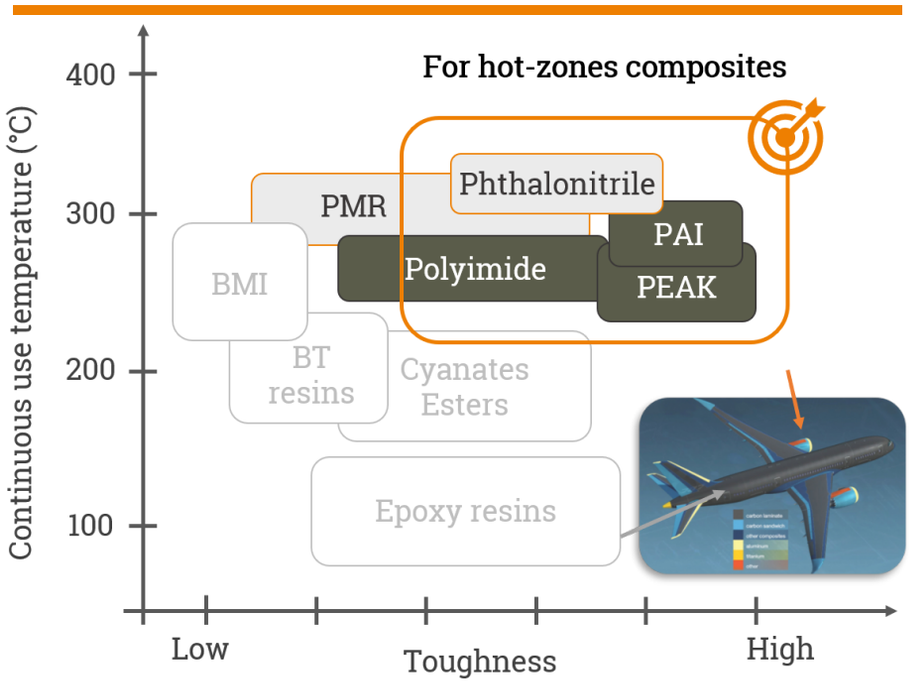


Figure 1: Overview of current heat-resistant resins - The dilemma between excellent mechanical properties and high continuous use temperature

Bismaleimides - BMI Resins

Bismaleimide resins had an important industrial development since the 1970's and presents today the highest production volume among high-performance resins. Their high glass transition temperature, thermal and oxidative stability and low flammability make them particularly attractive in the aeronautic sector. Moreover, the bismaleimides moieties can react according to different chemical reactions (Diels-Alder, Michael addition, free-radical reactions) and thus can be used in very different reaction mixtures. Last but not least, these molecules do not produce volatiles during these reactions and thereby the formation of voids into the materials is highly reduced.

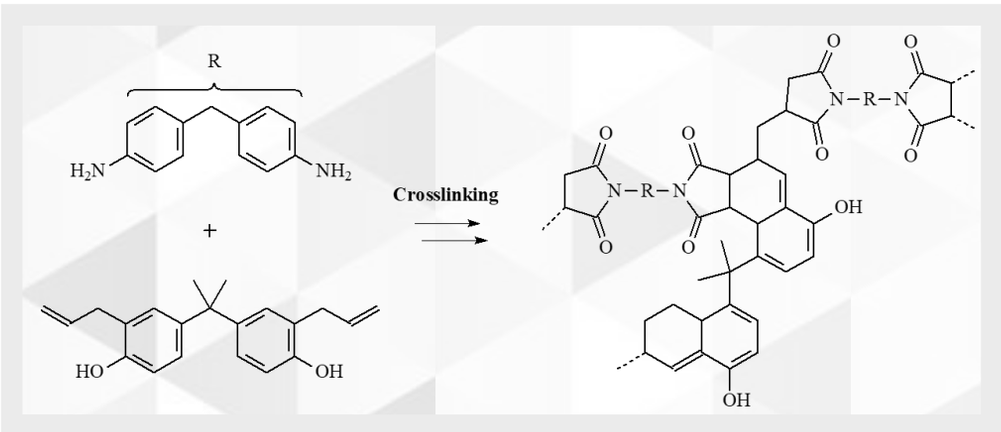
SPECIFIC POLYMERS

Tel : +33 (0)4 99 74 91 35
Fax : +33 (0)4 99 74 91 52

contact@specificpolymers.fr
www.specificpolymers.fr

However, due to the high crosslinking density, the materials are very brittle. First improvements were achieved with the introduction of succinimide rings bearing secondary amines (Kerimid 601®) but a loss in thermal stability was observed. Therefore, another strategy was implemented and corresponded to the co-reaction of the bismaleimides with di-allyl substituted bisphenols. This process led to the current benchmark BMI, thanks to the significant improvement of the resin‘s material properties.[1]

Figure 2: Simplified schematic representation of the synthesis of a second generation of BMI from 4,4-bismaleimidodiphenyl methane and diallyl-bisphenol A



Polyimides PMR Resins

Polyimides PMR (Polymerization of Monomeric Reactants) differ from BMI by their very high thermal stability with a continuous temperature use above 290°C. As a matter of fact, the PMR-15 have been particularly successful to replace titanium ducts for F404-engine. They are prepared by reaction between aromatic dianhydride ester acids and diamines in presence of a monoanhydride bearing a crosslinking group. The crosslinking reaction is achieved through two successive steps corresponding to (i) the deprotection of the maleimide end group by retro diels-alder fragmentation mechanism followed by (ii) crosslinking reactions through various addition reactions in between the maleimide moeities and the released cyclopentadiene.[2]

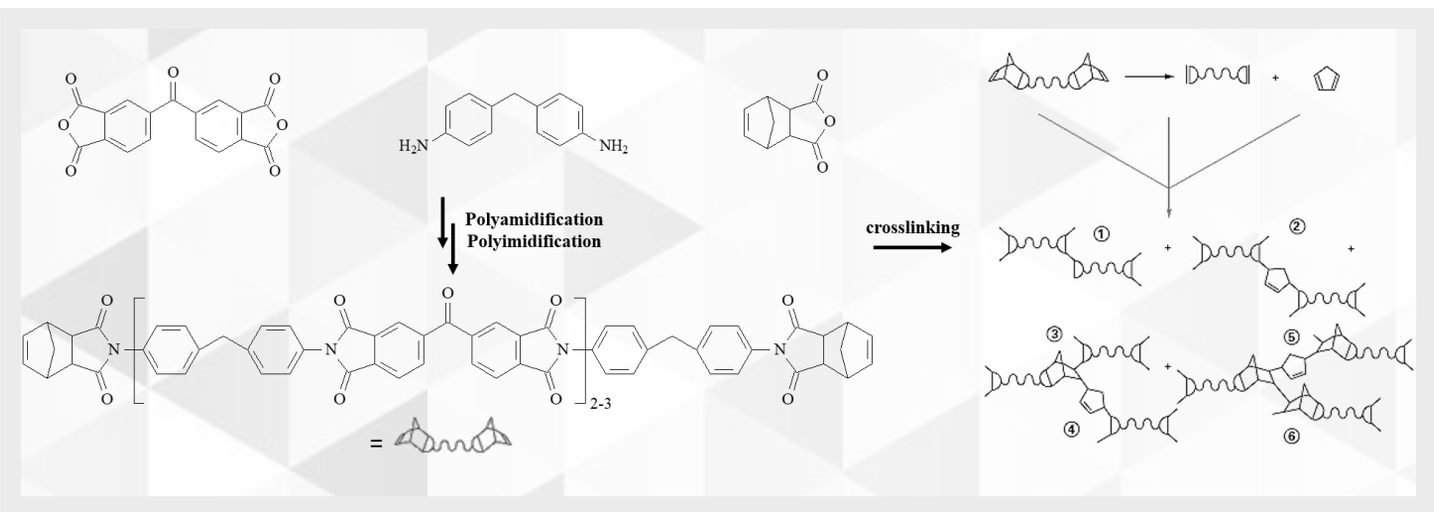


Figure 3: Synthetic pathway for the synthesis of PMR-15 resins

[1] Iredale, R.J., C. Ward, and I. Hamerton, Modern advances in bismaleimide resin technology: A 21st century perspective on the chemistry of addition polyimides. Progress in Polymer Science, 2017. 69: p. 1-21.

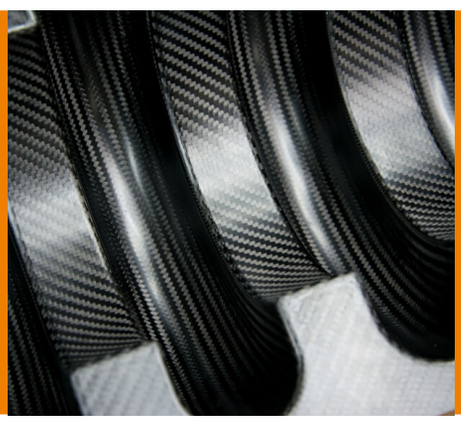
[2] Landis, A.L. and K.S.Y. Lau, 8 - High-Performance Polyimides and Related Thermoset Polymers: Past and Present Development, and Future Research Directions, in Handbook of Thermoset Plastics (Second Edition), S.H. Goodman, Editor. 1998, William Andrew Publishing: Westwood, NJ. p. 302-467.

SPECIFIC POLYMERS

Tel : +33 (0)4 99 74 91 35
Fax : +33 (0)4 99 74 91 52

contact@specificpolymers.fr
www.specificpolymers.fr

05 High Performance Thermosets



Because of the use of solvent and the lack of processability in RTM, further developments were achieved through the introduction of 4-phenylethynylphthalic anhydride end caps (PEPA) and led to the benchmarked PETI resins. These end caps enable to reduce the molecular weight and the viscosity of the resin while increasing the glass transition temperature (Tg). The PETI resins present temperature continuous use up to 340°C.

Phthalonitriles Resins

More recently, phthalonitriles have emerged as promising heat-resistant resins due to their outstanding properties. Thermal stability was proved to be particularly high with a thermal degradation onset at 500°C while presenting a low water uptake. Besides, the crosslinking reactions conduct to polytriazine, polyimine or polyphthalocyanine linkages without the release of volatile by-products.

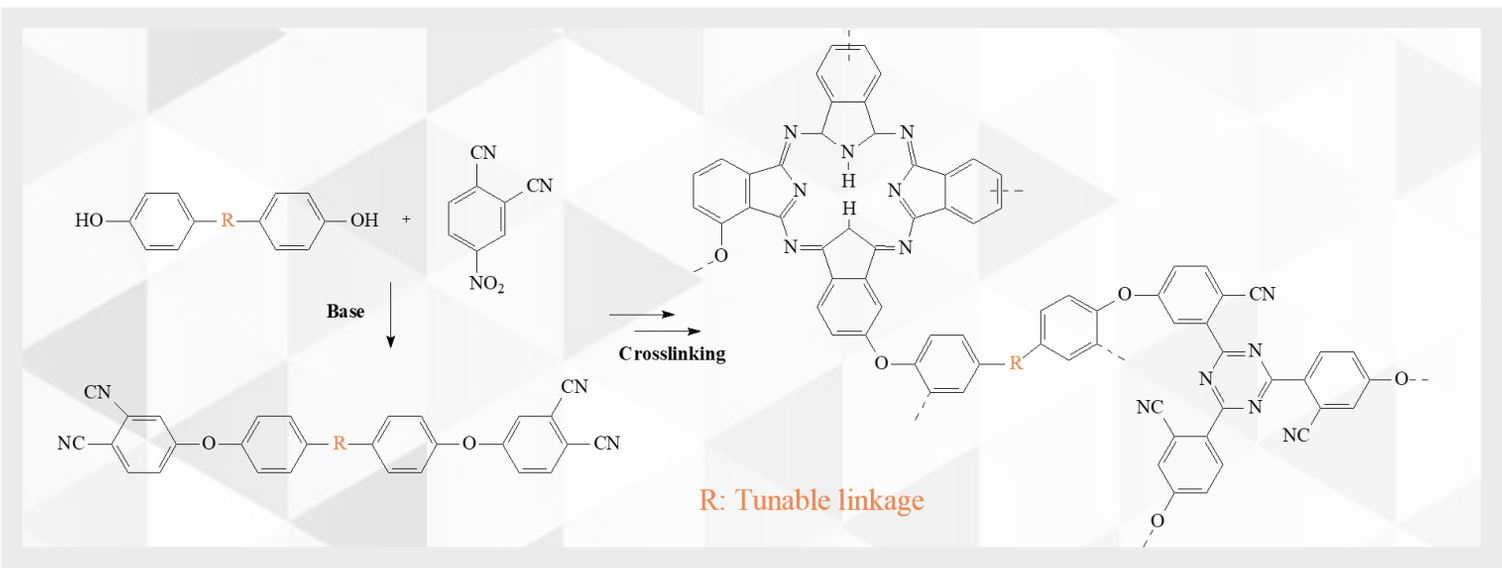


Figure 4: Synthetic pathway for the synthesis of tailor-made phthalonitrile resins

As for BMI, a second generation of phthalonitrile molecules has been implemented to improve their processability by introducing high thermal resistant oligomeric linkers in between the aromatic phthalonitrile moieties. These spacers are thermally stable oligomeric thermoplastics allowing the reduction of the macromonomers melting point from about 200°C to 70°C. Even though a slight loss in thermal stability is observed (<400°C), these resins still present excellent mechanical properties at 400°C.[3]

[3] Keller, T.M., T.R. Price, and J.R. Griffith, Synthesis of Phthalonitriles by Nitro Displacement. Synthesis, 1980. 1980(08): p. 613-613.

SPECIFIC POLYMERS

Tel : +33 (0)4 99 74 91 35
Fax : +33 (0)4 99 74 91 52

contact@specificpolymers.fr
www.specificpolymers.fr

Cyanate Esters Resins

Cyanate esters, that are widely used in the electronic field for their stable dielectric properties, are a more recent arrival among thermally stable resins compared to the BMI and PMR. They are the current newsmakers due to their very low moisture absorption (<2,5) and high thermal resistance. The crosslinking reaction between the cyanate ester groups lead to the formation of cyanurate ring.[4] The trimerization reaction occurs at 170°C-200°C and can be catalyzed with transition metal carboxylates.

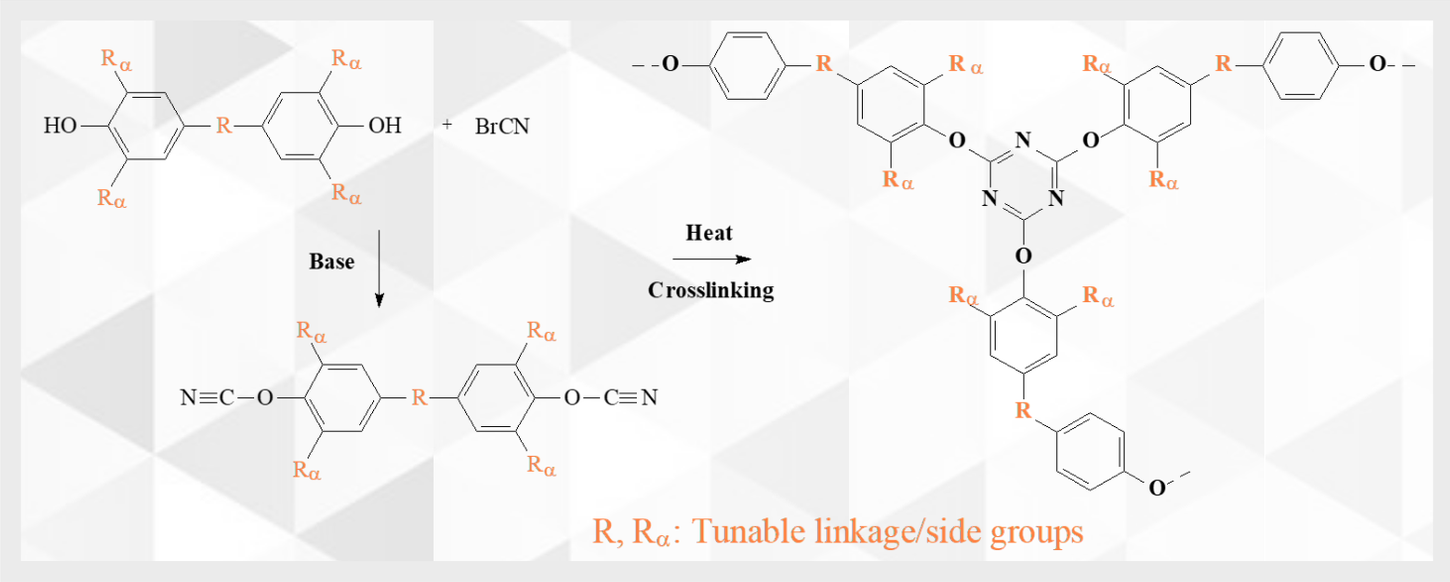


Figure 6: Synthetic pathway for the synthesis of tailor-made cyanate ester resins

Resulting thermosets are characterized by high glass transition temperature (up to more than 300°C) due to the high crosslinking density. However, this characteristic also induces brittleness. Particular attention is given in SPECIFIC POLYMERS to the development of the next generation of cyanates ester resins and their optimization in terms of toughness and maintain of the performances after ageing.

Custom services

SPECIFIC POLYMERS opens in 2019 a formulation & materials laboratory dedicated to tailor-made and high performance materials. SP wants to go a step further by helping its customers in all the aspects of materials development and by offering build-to-spec. materials synthesis services. Even if the targeted markets concern high added value materials, SP attaches a great importance to the industrial viability of proposed solutions. Thus, developments are most often based on the formulation of high-performance industrials products from various recognized suppliers with suitable SP tailor-made additives. SPECIFIC POLYMERS bases its material's developments on advanced understanding of structure-properties-performances relationships and in this aim initiates a material modelling activity to support experimentations.

[4] Cyanate Ester Resins Adapted from Cyanate Ester Resins, First Edition, in Wiley Encyclopedia of Composites. p. 1-15.