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HIGH PERFORMANCE PHTHALONITRILE RESINS

CHALLENGES AND ENGINEERING APPLICATIONS

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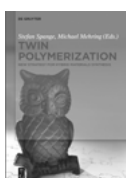**High-Performance Phthalonitrile Resins**

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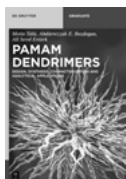ISBN 978-3-11-046828-1, e-ISBN 978-3-11-046974-5

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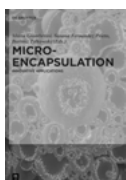ISBN 978-3-11-050067-7, e-ISBN 978-3-11-049936-0

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Preface

The search for high-strength, light-weight and high thermally stable and tough polymer materials has been going on since several years. Over the years, this quest resulted in the introduction of a host of materials ranging from phenolics to polyheterocyclics, polyimides, phenolic triazines, etc. Mostly, a single material cannot attain these property requirements that are most often contradictory. Then, it is an accepted practice to go for a blend of two or more polymer systems through either a physical blend or a co-reaction of the systems. The quest for advanced materials of this sort has now reached the door of polyphthalocyanines. They belong to the unique class of addition curable, high-temperature polymeric material having a great potential for applications in the fields of aerospace, marine, defence, etc. The research and development of phthalonitrile polymers flourished during the last two decades with the advent of studies on phthalonitrile systems with varying backbones, their blends and composites. Several studies have also been devoted towards the chemical structural modifications in phthalonitrile polymers in order to fine-tune their properties. The addition cure mechanism of phthalonitrile systems ensures that little or no volatiles are evolved during the curing, leading to highly cross-linked, void-free network polymers having good mechanical properties, outstanding thermo-oxidative stability, superior fire resistance and low water absorptivity compared to other conventional polymers. Excellent thermomechanical profiles in conjunction with their processability into void-free composites render phthalonitrile polymers the material of choice in contrast to the state-of-the-art high-temperature polymers such as PMR-15 and P-T resins. This area of research has witnessed tremendous progress in the recent years. The challenge of the system lies in achieving 100% curing at moderately low temperatures in a reasonable period.

Although there are a good number of research papers addressing various aspects, such as synthesis, polymerisation, reaction kinetics, blending and property evaluation, there has not been any serious attempt to consolidate all these information into a single book or a review article to analyse the potentiality of this material with respect to its synthesis feasibility and property tuning. In this backdrop this book, while trying to consolidate and analyse critically the tasks made in these directions so far, assumes a lot of importance.

The book analyses the recent development in the field of phthalonitrile polymers, taking into account the above aspects. Structural modifications through incorporation of thermally stable groups enabled the development of resin systems with tuneable properties. The structure–property relationship of these polymers, the role of different curatives and the corresponding postulated cross-linking mechanism are also examined. The methodologies to impart toughness to the system are also addressed. Processability and properties of the composites in relevant cases along with their application potentials are also highlighted. The relatively new

scenario of self-cure promoting phthalonitriles, which would extradite the long cure schedules required to attain the complete nitrile cure, has been given a little more focus in this treatise.

The book is divided in to five chapters. Chapter 1 describes the competence of phthalonitriles vis-à-vis other state-of-the-art polymers such as phenolic resins, epoxy resins, polyimides and cyanate esters.

Chapter 2 details the basic chemistry of phthalonitriles, including the cross-linking mechanisms and cure promoters and their reactions. Chapter 3 elaborates the structure–property relationships of phthalonitriles composed of different back-bones such as fluorine- imide- and benzoxazine-functional phthalonitriles. Chapter 4 focuses on the self-catalysed phthalonitrile systems, while Chapter 5 critically examines the blends and composites of phthalonitrile systems.

We have made all sincere efforts to include all significant advancements in phthalonitrile chemistry reported till date. The application potentials of these materials and future prospects of research and development in this area have also been highlighted in this book.

We thank all our well-wishers for their support and encouragements. Thanks are due to the Editorial Board and to the Director of Vikram Sarabhai Space Centre (VSSC) for giving permission to publish the book.

We thank our publisher De Gruyter for their interest in our proposal.

This book is dedicated to all our dear teachers and family members.

Prof. C. P. Reghunadhan Nair
Dr. Dhanya Augustine
Dr. Satheesh Chandran
Dr. Dona Mathew

Contents

List of Abbreviations

1,6-BDCN	1,6-*bis*(3,4-dicyanophenoxy)naphthalene
4-3′APPN	4-(3′-aminophenoxy)phthalonitrile
4-AmPN	4-aminophthalonitrile
6FPh	2,2-*bis*[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane
AAEPN	Aliphatic-aromatic ether phthalonitrile
AFPN	Amine-containing fluorine phthalonitrile
Al-N	Allyl novolac
APB	1,3-*bis*(3-aminophenoxy)benzene
APN	Amine-novolac phthalonitrile
AmPN	Aminophthalonitrile
APPN	4-(aminophenoxy)phthalonitrile
B3LYP	Becke, 3 parameter, Lee-Yang-Parr
BA-Ph	Phthalonitrile-containing benzoxazine
BPhA	2,2-*bis*[4-(3,4-dicyanophenoxy)phenyl]propane
BPhAPN	Bisphenol A phthalonitrile or Bisphthalonitrile ether of bisphenol A
BAPS	*Bis*[(amino phenoxy)phenyl]sulfone
BDS	*Bis*-[4-(3,4-dicyanophenoxy)phenyl]sulfone
BMI	Bismaleimide
BPhPN	4,4′-*bis*(3,4-dicyanophenoxy)biphenyl or (Biphenyl phthalonitrile)
BPhPR	Bispropargyl ether of bisphenol A
BTDE	3,3′,4,4′-Benzophenone tetracarboxylic acid
BZ-BPH	Bisphthalonitrile-containing benzoxazine units
BzPN	Phthalonitrile-functional polybenzoxazines
CAPN	Cured APN
CBPhPN-PR	Cured blend of BPhAPN and BPhPR
CNLPN	Char residue of cured NLPN
CNPN-PR	Cured NPN-PR
CNPR	Cured propargyl novolac
CPA	3,5-*bis*(3,4-dicyanophenoxy)aniline
DAPN	4-[4-(3,5-diaminobenzoyl)phenoxy]phthalonitrile
DBPA-Ph	Bisphthalonitrile monomer-containing allyl groups
DDS	4,4′-diaminodiphenyl sulfone
DEDPM	Diethynyl diphenyl methane
DFT	Density functional theory
DGEBA	Diglycidyl ethers of bisphenol A
DHBPN	Dihydroxy benzene phthalonitrile
DMAc	Dimethyl acetamide
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DOPO	9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DRPN	Dihydroresveratrol phthalonitrile
DSC	Differential scanning calorimetry
DTMPN	Triphenyl-based amine-catalysed phthalonitrile
Ea	Activation energy
EPN	Eugenol-based phthalonitrile

FW	Filament winding
GN	Graphite nanosheets
GO	Graphene oxide
HRR	Heat release rate
IL	Ionic liquids
ILSS	Interlaminar shear strength
LOI	Limiting oxygen index
LSS	Lap shear strength
m-APB	1,3-*bis*(3-aminophenoxy)benzene
MDA	Methylene dianiline
MPPN	4-(4-methyl phenoxy)phthalonitrile
MPPR	3-(4-methyl phenoxy)propyne
MW	Microwave
MWCNT	Multi-walled carbon nanotube
NAzPN	Phthalonitrile azo novolac resins
NLPN	Hydroxyl-phthalonitrile
NPN	Novolac phthalonitrile
NMP	*N*-methyl-2-pyrrolidone
NPN-OCN	Novolac resin bearing both −OCN and −CN groups
NPN-PR	Propargyl-phthalonitrile novolac
ODA	Oxydianiline
PAS	Polyaryl sulfone
p-BAPS	*Para-bis* [4-(4-aminophenoxy)phenyl]sulfone
PBZ	Polybenzoxazines
PEEK	Polyether ether ketone
PEI	Polyetherimide
PEKK	Polyether ketone ketone
PEN	Poly(arylene ether nitrile)
PES	Polyether sulfone
PF	Phenol formaldehyde
PN	Phthalonitrile
PIPN	Phthaloimido phthalonitrile
PMDA	Pyromellitic dianhydride
PMR	Polymerisation of monomeric reactants
PNBI	Benzimidazole-containing phthalonitrile
PPS	Polyphenylene sulphide
PR	Propargyl
PT	Phenolic triazine
PyPN	Pyridine-containing phthalonitrile
PZ	Polyphosphazene
RIM	Resin infusion moulding
RPN	Resveratrol phthalonitrile
RTM	Resin transfer moulding
SEM	Scanning electron microscope
SiPN	Silicon-containing phthalonitrile
SiC	Silicon carbide
SKPN	Sulfone-ketone phthalonitrile

SNS-PN	4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl)phthalonitrile
$T_{5\%}$	5% Mass loss temperature
Tg	Glass transition temperature
T_i	Initial cure temperature
T_{peak}	Cure exotherm peak temperature
T_{IG}	Time-to-ignition
xGnP	Exfoliated graphite nanoplatelets

1 Phthalonitriles and state-of-the-art high-performance thermosets

1.1 Introduction to high-performance polymer systems

Rapid pace of advances in modern science and technology demand newer and special materials. Meeting these requirements depends, to a great extent, on the ability to develop tailored materials. High-performance polymers and composites are highly versatile and they can be tuned to the desired forms/formulations to meet the ever-increasing demands of modern technology. The application of polymer has crossed the barriers of household to enter high-tech areas such as electrical, electronics, aerospace and communication satellite-mediated ultra-fast communication. Space and interplanetary travel became a reality, thanks to the phenomenal growth in polymer materials.

High-performance polymers have found widespread utility in everyday life to high-end applications. They have revolutionised the outlook of industrial and aerospace arena and literally materialised the major requirements such as weight reduction and minimal energy dissipation. These are accomplished by architecting monomers and polymers with tailorable functionality, reactivities and backbones. By virtue of the higher strength-to-weight ratio, many polymer matrix composites could outsmart metallic structures [1–3].

By definition, high-performance polymers are used in applications that demand service at elevated temperatures while maintaining their structural integrity. Chemical resistance and retention of physical and mechanical properties at high temperature are highly essential. Development of heat-resistant polymers and high-performance polymer matrix composites that can function above 250 °C for long duration has been an area of interest for more than a decade. The ability of polymers to attain structural features such as heterocyclic, rigid backbones after cross-linking makes them suitable candidates for applications in extreme thermal conditions. Typically, high-performance polymers display a glass transition temperature (T_g) of >200 °C and a melting temperature of >450 °C [4–8].

As mentioned earlier, the increased demand for high-performance materials in modern aircrafts and space vehicles could lead to explorations for widening their temperature withstanding capability at still higher temperature regimes. Today, there are many advanced thermosets and thermoplastics that exhibit excellent thermal performance even at very stringent conditions. Some of the notable systems are thermosets such as epoxies, phenolic resins, bismaleimides (BMI), cyanate esters, polyimides (PI), polymerised monomeric reactant (PMR), phenolic triazine (PT) resins and thermoplastics like polyether sulfone (PES), polyether ether ketone (PEEK), polyetherimide (PEI) and polyether nitrile [9–13]. The latest thermoset entry in this array is phthalonitrile (PN) resins.

Prelude to the discussion on PN polymers and their chemistry and technology, it is felt appropriate to have a brief discussion on the state-of-the-art thermally stable polymeric resins.

1.2 State-of-the-art high-performance polymers

1.2.1 Phenol formaldehyde resins

Phenolic resins are synthesised by the step-growth polymerisation of formaldehyde and phenol in the presence of an acid or a base catalyst. Novolacs are formed under acidic conditions with an excess of phenol to formaldehyde (HCHO) stoichiometry (1.5–1.7) in the feed, whereas resoles are synthesised under basic conditions with an excess of formaldehyde (phenol: HCHO = 1:1.6) in the feed [14–16]. Novolac requires the presence of cross-linking agents such as hexamethylene tetramine, whereas resoles can be cured by heating [17–19]. Synthetic schemes for novolac and resoles are shown in Schemes 1.1 and 1.2 respectively.
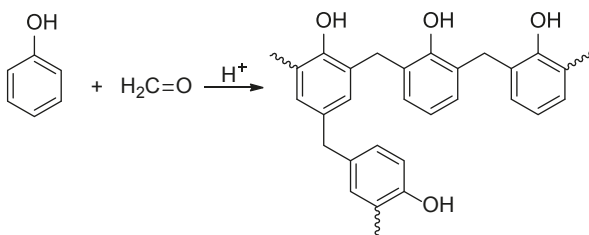
Scheme 1.1: Synthesis of novolac.

The advantages of phenolic resins include excellent dimensional stability with a constant usage temperature range of 150–160 °C, excellent resistance to chemicals, moisture, heat and fire. The main areas of application include insulation products, abrasive and friction lining materials. Because of their high aromatic content, phenolic resins absorb a lot of heat for their thermal degradation, and hence it is used as an ablative material in re-entry spacecarfts. Phenolic resins are also used as an alternative to conventional precursor (pitch and tar) materials for the production of carbon-based engineering materials (e.g., glassy carbon, carbon fibres and carbon–carbon composites) [14, 20, 21].

Generally, phenolic-type resin systems undergo polymerisation through condensation-type polymerisation reaction. This causes defects in their composites as composites are prone to voids caused by the release of certain other molecules such as water vapour and formaldehyde during cure leading to the premature failures at the point of their application. Hence, phenolics have the inherent drawback of poorer
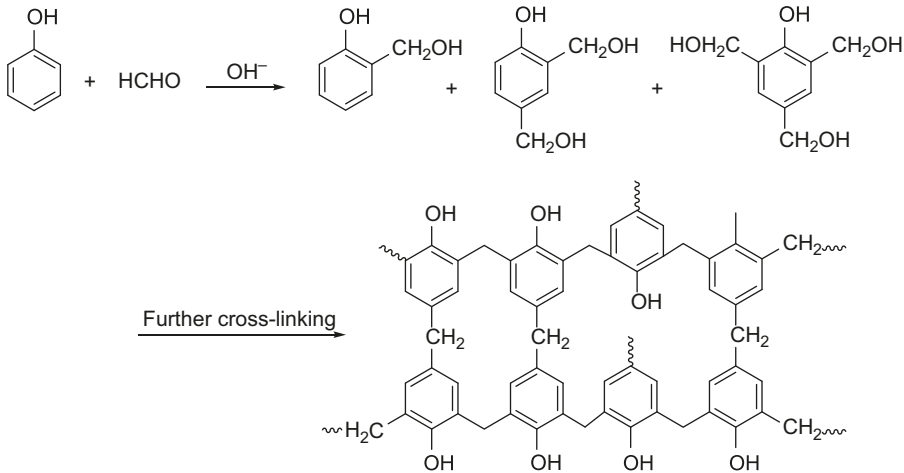
Scheme 1.2: Synthesis of resole and its cross-linking.

mechanical properties than those of epoxies and most other high-performance resins. An additional step to be included in the phenolic composite processing ensures the removal of water molecules by venting, and this can mainly be employed only for compression-type mouldings. Therefore, phenolics are not typically processed using resin transfer moulding (RTM), which is the most common type of composite moulding employed for thermosets. To alleviate these shortcomings, phenolic resins with addition-curable nature were developed and well accepted. Addition-curable phenolics with different chemical modification are available and some of them are realised as follows: (i) incorporation of thermally stable addition-curable groups onto novolac backbone, (ii) structural modification (transformation) involving phenolic hydroxyl groups, (iii) curing of novolac by suitable curatives through addition reactions of OH groups and (iv) reactive blending of structurally modified phenolic resin with a functional reactant. Allyl-functional phenolics, bisoxazoline–phenolics, phenolic resin–epoxy systems, propargyl ether and ethynyl novolacs and so on belong to the class of addition-curable phenolic resins with improved thermal and pyrolysis characteristics (Scheme 1.3). They are potential candidates as matrices in carbon/carbon composites for thermostructural applications [22].

1.2.2 Epoxies

Epoxy resins are the most versatile class of thermoset polymers in modern industry. The chemical constitution of an epoxy resin is identified by more than one α-epoxy group (oxirane rings) situated terminally, cyclically, or internally in a molecule which is converted into an infusible hard mass by curing reaction with a wide variety

Allyl novolac

Bisoxazoline-phenolic network

Propargyl novolac
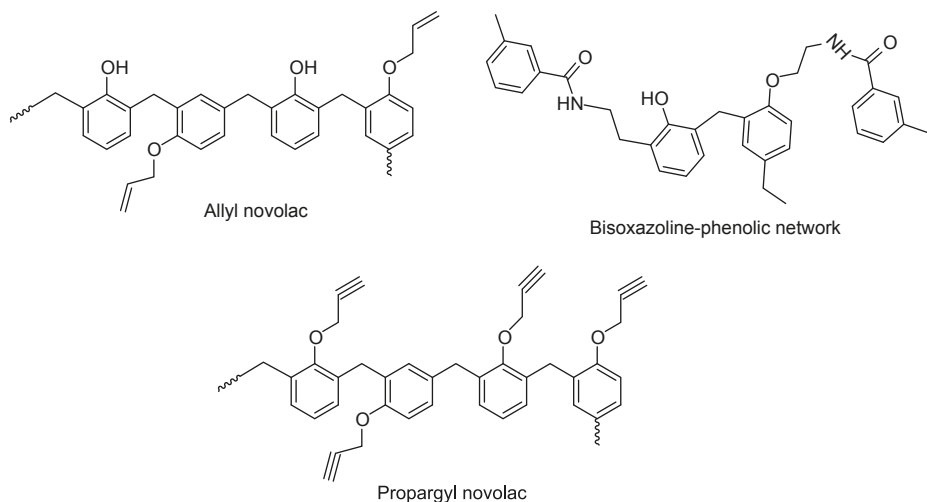
Scheme 1.3: Various addition-cure phenolic resins.

of curing agents. Typical synthesis of epoxy resin is shown in Scheme 1.4. The outstanding properties of the epoxy thermosets include good mechanical strength and excellent chemical and corrosion resistance. Other important features include absence of volatiles, low shrinkage on cure and good dimensional stability [23–25]. Epoxy resin with structural variations such as diglycidyl ethers of bisphenol A, epoxy novolac and cycloaliphatic epoxides are well marketed for the diverse applications.
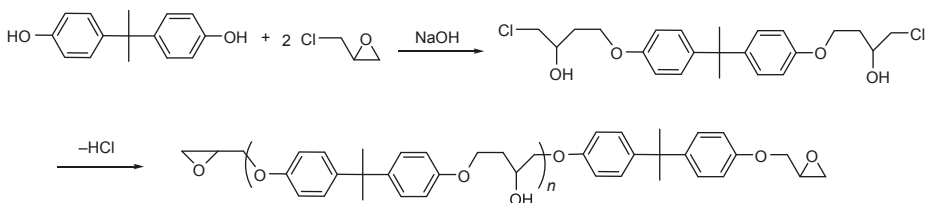
Scheme 1.4: Typical synthesis of an epoxy resin.

Epoxies are cross-linked using hardeners. These molecules contain reactive hydrogen that can cause a catalytically induced polymerisation through addition reaction by reacting with the epoxide groups to obtain the final cross-linked structure. The most common type of hardeners include aliphatic amines, cycloaliphatic amines, polyamides, aromatic amines, anhydrides, phenols, thiols and latent hardeners (e.g., Lewis acids). The type of hardener used affects the final properties of the cured resin, and thus the composite [26–32]. The hardener to the base resin ratio used is

critical to ensure a complete reaction. Otherwise, the resin will neither fully cure nor attain its full properties. Meter/mix-dispense equipment is used widely now to automate and accurately control this mixing of resin. Many aerospace applications use amine-cured, multifunctional epoxies that require cure at elevated temperatures and pressures leading to the processing difficulty. These resin systems being brittle due to the high degree of cross-linking, toughening by means of thermoplastics and reactive rubber compounds are commonly explored in epoxy chemistry [33, 34].

1.2.3 Polyimides

Polyimides (PI) constitute a class of high-temperature polymer with a cyclic imide backbone that imparts outstanding thermal stability. They are mainly used in electronic and aerospace industries. Their synthetic route includes the reaction of a dianhydride with an aromatic amine (Scheme 1.5). A polyamic acid intermediate is formed in the first step which further polymerises to form PI [35–40].

Pyromellitic dianhydride   Oxydianiline   Polyamic acid

Polyimide
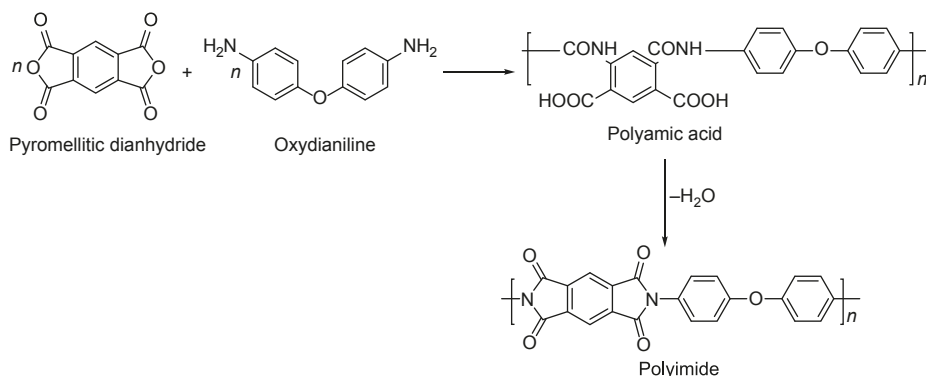
Scheme 1.5: Synthesis of PI.

The fully cured PIs are intractable and they are often commercialised in the form of polyamic acid precursor solutions. By heating, the solvent is removed and condensation reactions are initiated forming the fully cured imide resin. High-molecular-weight PIs formed by condensation routes undergo decomposition prior to its melting. Some of the examples for condensation PIs are Torlon®, Kapton® and Vespel® SP-1 [41, 42].

    The infusibility and insolubility of imide polymers have limited the full utilisation of these materials as high-temperature matrix resins and were of little commercial interest. To circumvent this problem, the PMR approach has been adopted. PMR family of PIs is formed by impregnation of the reinforcing fibres with monomer combinations dissolved in low-boiling alkyl alcohol (Scheme 1.6). At high
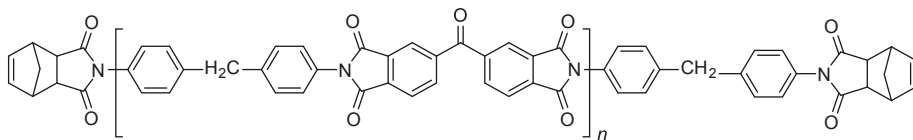
Scheme 1.6: Typical structure of a PMR resin.

temperature, the monomers undergo in situ condensation and addition cross-linking to form thermally stable PI. The first generation of PMR resin was designated as PMR-15 and the second-generation PMR-II. The monomer composition of PMR-15 includes the dimethyl ester of 3,3′,4,4′-benzophenone tetracarboxylic acid (BTDE), methylene dianiline (MDA) and monoalkyl ester of 5-norbornene-2,3-dicarboxylic acid in a molar ratio of 2.087:3.087:2. In the temperature range of 121–232 °C, norbornene end-capped low-molecular-weight imide prepolymer is formed by way of in situ dehydration. Norbornene end-caps will undergo addition polymerisation at high temperatures without the formation of any by-products. The second-generation PMR resins used the perfluorinated isopropylidene analogue of BTDE known as 6FDE diethyl ester of 4,4 -(hexafluoroisopropylidene) diphthalic acid and phenylene diamine. PMR-15 formulation has shown good high-temperature performance, but their wide applicability is limited due to the mutagenicity of MDA used for their synthesis and high cost for fabricating engine components due to processing difficulties. Nadic groups polymerise through carbon–carbon double bond and the resulting aliphatic cross-linking centres are easily susceptible to thermo-oxidative degradation. Efforts have been made to make PMR without using MDA. LARC™ RP46 resin was developed as an alternative to PMR-15 resin by replacing MDA with 3,4′-oxydianiline. Similarly, other aromatic amines such as 2,2′-dimethyl benzidine and 2,2′,6,6′-tetramethyl benzidine were also tried as a replacement for MDA. However, such replacement often resulted in reduction of the thermo-oxidative stability of the PI product [42–50].

Increase in molecular weight of prepolymers increases their softening temperature and viscosity which adversely affects their processing. Therefore, low-molecular-weight resins are preferable from a processing point of view. However, they often cannot match the thermo-oxidative stability and toughness offered by high-molecular-weight resin formulations. Hence design of high-molecular-weight PMR prepolymer with better processability is a great challenge.

1.2.4 Bismaleimides

BMI class of polymers are derived from monomers/oligomers with maleimide terminations. Maleic anhydride reacts with aromatic diamines forming bismaleamic acid, which undergo dehydration to form BMI. They exhibit thermal stability

equivalent to PI and can be fabricated under epoxy-like conditions. The commercial BMI resins are mostly made from MDA. The typical synthesis scheme of BMI is represented in Scheme 1.7.
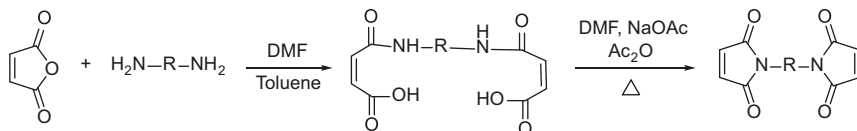
Scheme 1.7: Typical synthesis scheme of BMI (DMF:dimethyl formamide).

BMI derived from aromatic diamines and those having electron withdrawing groups in the backbone increases the melting point. The high cross-link density and aromatic nature of cured BMI resins makes them highly brittle [51–57]. The effective method to toughen the BMI resin is to copolymerise with elastomers and reactive diluents. Generally, triallyl cyanurate, divinyl benzene, amino-terminated acrylonitrile–butadiene rubber, carboxy-terminated acrylonitrile–butadiene rubber and allyl-type reactive resins are used as BMI toughening agents [58–70]. Different structural modifications are attempted to design BMI with desirable properties. Incorporation of ether linkages into the polymer chain provides flexibility but leads to reduction in T_{g} and failure in property retention at elevated temperatures. Flame resistance of BMI with phosphorus-containing segments is superior relative to the base BMI resins. Maleimide end-cappings to the high-performance thermoplastics like polyether sulfide is an effective way to achieve improved toughness and high thermal resistance (Scheme 1.8).
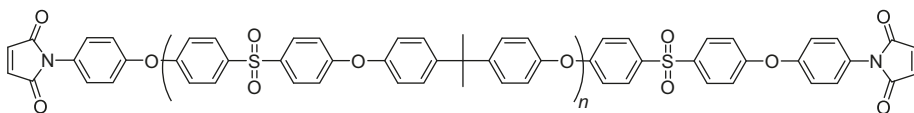
Scheme 1.8: Structure of a maleimide-terminated PES.

1.2.4.1 Alder-ene polymers

Despite the good attributes of high thermomechanical profile, application of BMI polymers in high-performance composites has been limited due to the inherent brittleness of the system [71, 72]. There have been many attempts such as reactive blending of BMI with olefinic compounds to reduce the brittleness, but staking the thermal stability of the matrix. Allyl-functional monomers and polymers help improve the processability of the polymers and toughness of the resultant

networks, rendering the BMI system more suitable for high-performance composites [73, 74]. The allyl compounds react with maleimide groups via the Alder-ene reaction. The main reaction sequence of the Alder-ene polymerisation is as follows:

1. In the 100–200 °C range, the maleimides and allyl monomers react via ene reaction to form ene adduct. In addition, the hydroxyl groups undergo etherification by hydroxyl dehydration.
2. The unsaturated ene adduct intermediate undergoes Diels–Alder-type reaction with BMI to give the *bis-* and *tris-*adducts. The intermediate step (Diels–Alder) is sometimes referred to as Wagner-Jauregg reaction. Along with the Alder-ene reaction, at higher temperatures, the copolymerisation of maleimides and allyl monomers also occurs.
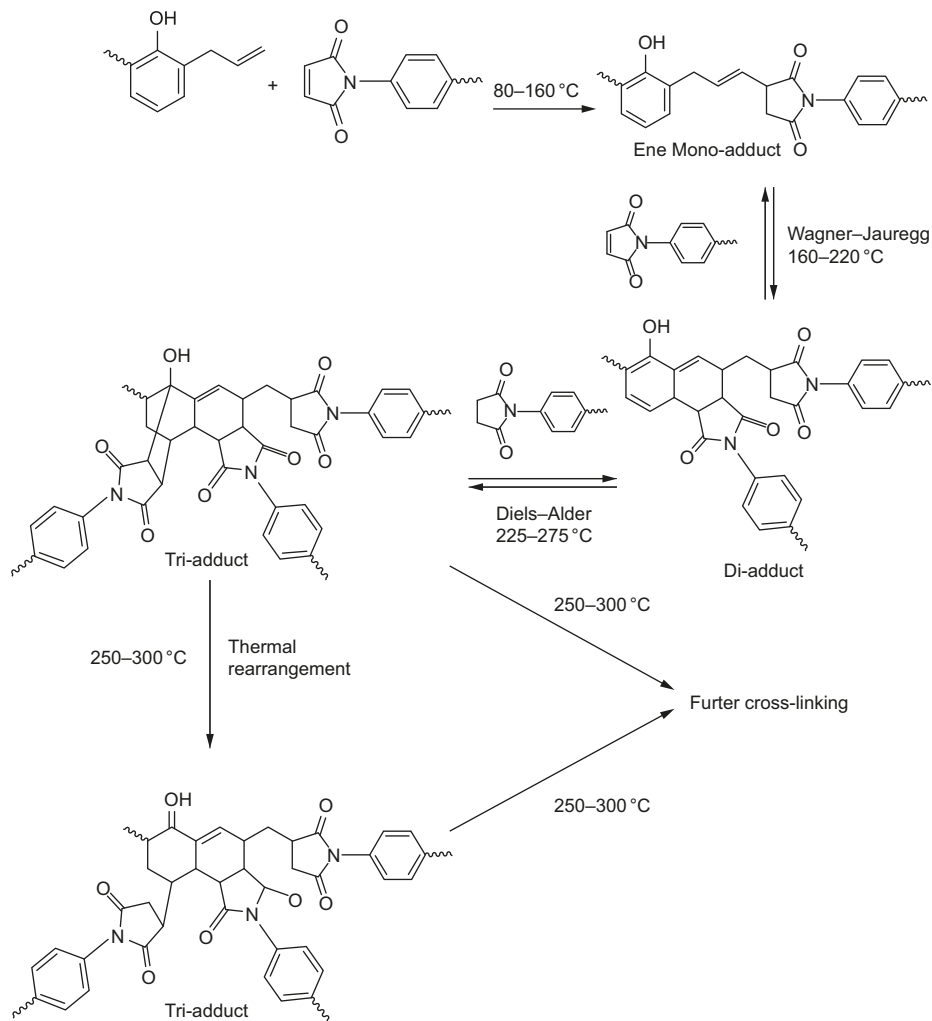
The reaction sequence of Alder-ene polymerisation is represented in Scheme 1.9.

Alder-ene polymers offer an intermediate material in temperature performance between epoxies and PI because of their capability of performing at temperatures up to 230 °C and ability to be fabricated using epoxy-like conditions, without the evolution of void-producing volatiles [4, 76].

1.2.5 Cyanate esters

Cyanate ester resins constitute an important class of advanced thermosets with good mechanical properties, low coefficient of moisture expansion and low dielectric constants. They are prepared by the reaction of cyanogen halides with phenol in the presence of a tertiary amine (Scheme 1.10).

The curing of cyanate ester resin proceeds via thermally activated addition reaction involving simple cyclotrimerisation to form PT networks without the formation of volatile by-products [77–79]. Side reactions leading to the formation of dimer and higher oligomers occur to a minor extent. The autocatalytic reaction occurs without any catalyst at temperature above 200 °C. Catalytic trimerisation of cyanate groups is done using transition metal catalyst or chelates in the presence of an active hydrogen source such as nonylphenol. Only a minute amount of catalyst is needed to facilitate the cross-linking reaction. It gives conversions greater than 98% and results in a polycyanurate thermoset. The resulting network structure shows high toughness and high T_g in the range of 290–300 °C, a combination of properties that is not usually achieved in conventional thermosets. This can be ascribed to the triazine phenyl ether linkages, low cross-link density and apparent high free volume in the cured network [80–82]. For certain critical structural applications, further improvement in toughness can be achieved by blending cyanate ester resins with elastomers, engineering plastics and epoxies. The cyanate esters have the processability similar to that of epoxy resins and thermal properties similar to phenolic systems. Cyanate ester homopolymers exhibit twice the fracture

Scheme 1.9: Reaction sequence of Alder-ene cross-linking and network formation. Adapted from X. Xiong, P. Chen, J. Zhang, Q. Yub and B. Wang, *Thermochimica Acta*, 2011, 514, 44 [75].

toughness of epoxies and certain cyanate ester–epoxy formulations offer desirable properties applicable in both electronics and structural composites.

Multifunctional cyanate ester based on phenolic novolac is commercialised in the trade name Primaset® (PT) resins which undergoes thermal cross-linking similar to that of dicyanate monomers [19]. They offer low shrinkage and can thermally cross-link to form void-free networks. Their cured network is mainly comprised of polycyanurate structures attached to novolac backbone with T_g greater than 300 °C and onset of aerobic thermal degradation in the range of 440–450 °C. PT family of
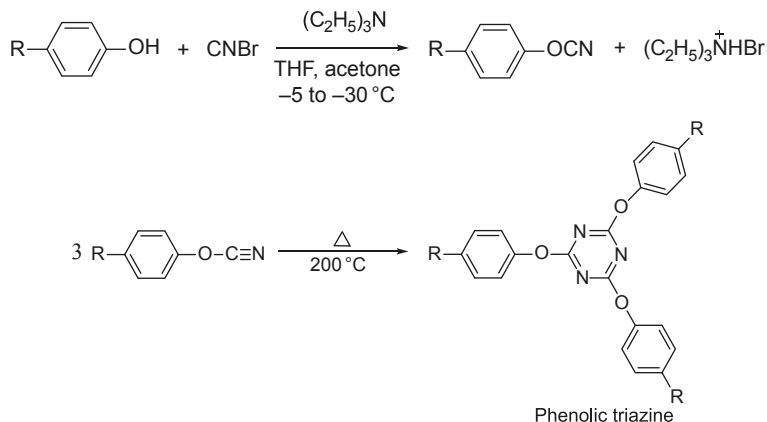
**Scheme 1.10:** Synthesis and curing of cyanate esters.

resins show consistency that ranges from low viscous liquids to semisolids and their gel temperatures can be tuned by catalysis using a host of materials. They have broad processing flexibility and are commercialised under the trade name Primaset® PT-15, PT-30, PT-60 and PT-90 [83–85]. However, the extensive commercialisation of PT systems is somewhat restricted due to their poor shelf-life and inconsistency in cure behaviour due to catalysis by the impurities during its synthetic stage. As their decomposition products include toxic cyanic acids (HCNO), their excellent thermal performance couldn't be well exploited in the design of ablative thermal protection systems [77].

1.2.6 Polybenzoxazines

Polybenzoxazines (PBZ) belong to the addition-cure phenolics family, which combines the thermal properties and flame retardance of phenolics and the mechanical performance and molecular design flexibility of epoxies. The PBZ overrides several shortcomings of conventional novolac and resole-type phenolic resins while retaining their benefits. The molecular structure of PBZ offers superb design flexibility that allows properties of the cured material to be controlled for specific requirements of a wide variety of individual requirements (Scheme 1.11) [86–89].

The resin permits development of new applications by utilising some of their unique features such as:
– Near-zero volumetric change upon polymerisation
– Low water absorption
– T_g much higher than cure temperature
– Fast mechanical property build-up as a function of degree of polymerisation
– High char yield
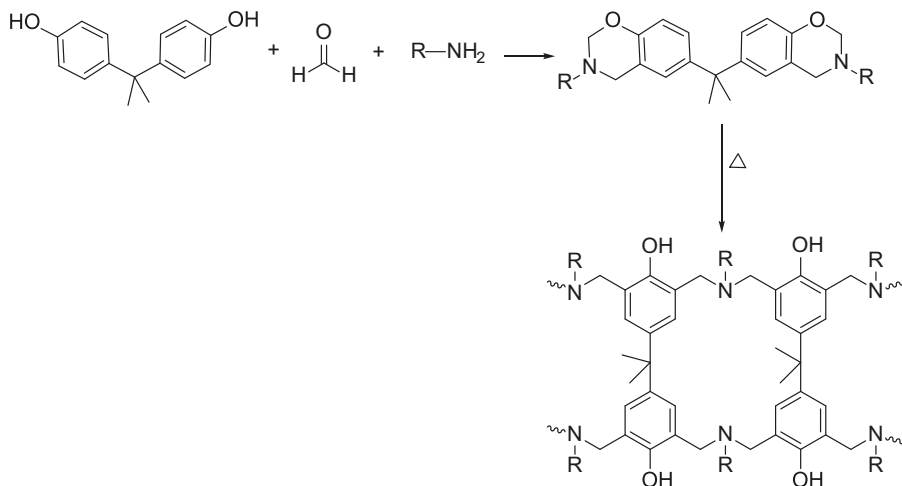
Scheme 1.11: Synthesis and polymerisation of benzoxazines.

- Low coefficient of thermal expansion
- Low viscosity
- Excellent electrical properties

PBZ present a resin system with the highest tensile properties, and T_g can be boosted to as much as 340 °C through proper choice of the precursor phenol. Dynamic mechanical analysis reveals that these candidate resins for composite applications possess low cross-link densities yet have high moduli and T_g. Long-term water immersion studies indicate that these materials have a low rate of water absorption and low saturation content. PBZ are cured usually in the temperature window of 160–220 °C. The polymers exhibit T_g in the range of 160–340 °C depending on the structure and have higher thermal stability. The high-thermogravimetric analysis (TGA) decomposition onset temperature (for dihydroxy benzophenone–aniline system, it is 400 °C) is attributed to the very strong intramolecular H-bonding between phenolic OH and the Mannich bridge. Char yield as high as 82% has been claimed for certain compositions. [90, 91]

The ring-opening polymerisation of these new materials occurs with either near-zero shrinkage or even with a slight expansion upon cure. It is proposed that the volumetric expansion of the Benzoxazine (BZ) resin is mostly due to the consequence of molecular packing influenced by inter- and intramolecular hydrogen bonding. The role of hydrogen bonding on the volumetric expansion has been studied systematically by changing the primary amine used in the BZ monomer synthesis. PBZ have the lowest heat release during combustion and is, therefore, more flame resistant, surpassing that of phenolics and PEI, the current aerospace matrices of choice. Another

advantage of PBZ is that it can be reactively blended with a host of matrices including cyanate ester, epoxies and so on, which form excellent combination matrices [92, 93].

1.2.7 Polyetherimide

Polyetherimides (PEIs) are considered as high-performance plastics due to their exceptional mechanical and thermal properties. However, they are intractable and difficult to mould to their end-products. Modified version of imide resin is PEI, where the processibility issue is amended by incorporating flexible ether linkages. Ether bonds in PEI molecular chain provides balanced properties with enough flexibility to allow good melt processibility and can retain the aromatic imide properties [94, 95]. The first member of this family of PEI is introduced by the General Electric Company under the trademark ULTEM® resin. PEI resin compositions can be tailored to provide materials having T_g ranging from −150 to −300 °C. They resist most chemicals, including hydrocarbons, alcohols and halogenated solvents, and have excellent long-term creep resistance. In many cases, they can replace metals and other high-performance materials in structural applications. The electrical properties are of excellent stability under variable temperature, humidity and frequency conditions. Their main synthetic route is nucleophilic aromatic nitro displacements by aryloxide ions. In the first stage, cyclisation reaction is between nitrophthalic anhydride and diamine to form bisimide rings with nitro groups. Then, it is treated with bisphenolates to form PEI (Scheme 1.12) [94].
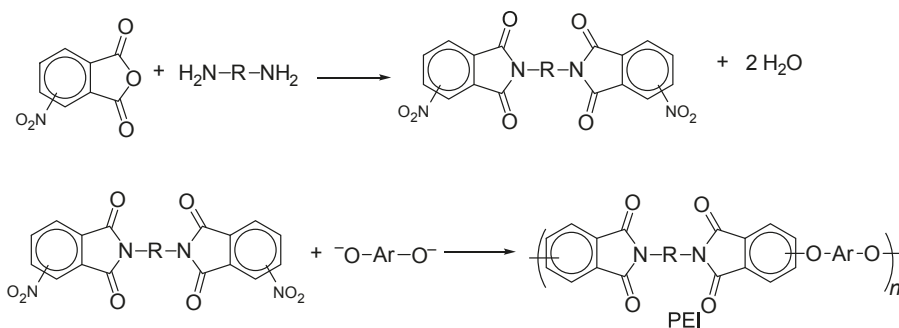
Scheme 1.12: Synthesis of PEI.

1.2.8 Polyether ether ketone

PEEK is a semicrystalline polymer that has gained wide attention as an engineering thermoplastic with outstanding properties. It possesses excellent resistance amidst a

wide range of chemical environments, even including high temperatures and can only be dissolved in concentrated nitric acid or sulfuric acid. It displays good friction as well as wear properties enabling a long service life and exhibit very good hydrolysis resistance. The outstanding high-temperature resistance makes these polymers an ideal choice when the process temperatures go beyond the limit of what conventional plastic materials can withstand. Also, PEEK polymers exhibit excellent solvent resistance, superior mechanical properties, high toughness and excellent thermo-oxidative stability [96, 97]. These features render them highly attractive as high-performance toughening agent as well as for advanced high-performance matrices without compromising their desirable attributes [98, 99]. However, the modulus of PEEK decreases evidently at elevated temperatures because of a relatively low T_g around 140–145 °C, which limits its applications at high temperature. One problem associated with thermoplastic toughening is the poor phase adhesion between the thermoset matrix and the toughening agent because of their poor compatibility [100]. Thus, thermoplastic-toughened thermosets form homogeneous blends in the uncured state and undergo phase separation on curing [101]. In order to circumvent the phase separation-related issue, the processing of blends is experimented using PEEK with terminal-functional groups and also with bulky pendant groups [102].

1.3 Phthalonitrile polymers

PN polymers are considered as potential candidates as matrices for high-temperature performing composites are widely used for the technologically advanced areas of aerospace and aircrafts. These application areas are dominated by special polymers such as polybenzimidazole, PT resins and PMR systems. However, these systems with T_g, of the order of >300 °C were short lived and have drawbacks such as processability. In this backdrop, PN polymers emerged with several advantages such as:

- High T_g (350–400 °C)
- Moderately good processability
- Unlimited shelf-life for the prepolymer
- Outstanding thermo-oxidative stability
- Good retention of mechanical properties at elevated temperatures (>50%)
- Low water absorptivity (<1%)
- Superior fire resistance (limiting oxygen index >50)

With these advantages, PN polymers emerged as an important high-performance thermoset which has high-tech applications in the fields ranging from electronics to military and aerospace area. They have been developed to address the shortcomings of currently available thermosetting resins (Table 1.1). Their main attributes include exceptional thermal and thermo-oxidative stability, superior mechanical property retention over wide temperature ranges and fire and chemical resistance [103–105].

Table 1.1: Comparison of high-performance thermosets.

Property	Epoxy	Phenolics	Toughened BMI	Cyanate ester	PN
Density (g/cc)	1.2–1.25	1.24–1.32	1.2–1.3	1.1–1.35	1.2–1.3
Max. use temperature (°C)	180	200	~200	150–200	>370
Tensile strength (MPa)	90–120	24–45	50–90	70–130	85
Tensile modulus (GPa)	3.1–3.8	3–5	3.5–4.5	3.1–3.4	4.4
Elongation (%)	3–4.3	0.3	3	2–4	1.2
Dielectric constant (1 MHz)	3.8–4.5	4–10	3.4–3.7	2.7–3.0	–
Cure temperature (°C)	Room temperature to 180	150–190	220–300	180–250	200–350
Cure shrinkage (%)	>3	0.002	0.007	~3	–
TGA onset (°C)	260–340	300–360	360–400	400–420	>450
T_g (°C)	150–220	170	230–380	250–270	~500
Fracture energy (G_{IC}) (J/m^2)	54–100	–	160–250	–	120–130
Fracture toughness (K_{IC}) (MPa m$^{1/2}$)	0.60	–	0.85	–	–

Adapted from C.P.R. Nair, *Progress in Polymer Science*, 2004, 29, 401 [22].

A fully cured PN system retained long-term mechanical properties even up to 370 °C [106]. More significantly, there is no indication of a glass transition or softening up to 500 °C [107]. The uncured resin has a low melt viscosity that allows it to be used in an RTM process [108].

In many cases, their application horizon is limited mainly because of their inherent brittleness coupled with their need for prolonged duration of heating at elevated temperatures. The prominent issue that remains still unresolved is, many of the PN-based systems need very high cure temperature as the stable C≡N needs very high thermal activation. To overcome these drawbacks, extensive research is actively pursued to modify this class of polymers mainly by altering their cure chemistry and adopting backbone structural variations. In this backdrop, our attempt to compile the advances in the field of PN chemistry and to make a comprehensive overview of the recent developments gains significance. An in-depth overview of PN monomers, polymers, blends, curatives and composites, and our critical views on these systems are detailed in the later chapters.

In this chapter, an overview of the high-performance thermosets is given with emphasis on their synthesis and cure chemistry and application potential. The

application areas of these polymers and the derived products are so exhaustive. All these high-performance polymers and their composites are highly versatile and they can be tuned to the desired forms/formulations to meet the ever-increasing demands of technology. A comparison of their properties reveals the importance of each in its own area. PNs are considered as the Trojan horses in this scenario, poised to make their entry in a very significant way.

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2 Basic Chemistry and general remarks

2.1 Introduction

This chapter deals with the diverse chemistry of phthalonitrile (PN) that is responsible for the versatility of these systems. The understanding of the basic chemistry that led to the development of the PN polymer systems has been dealt with in detail.

2.2 PN monomers, oligomers and prepolymers

In 1930, much interest was shown on the formation of thermally stable phthalocyanine derivatives, and later, attempts were undertaken to see whether this unit might be incorporated into a polymeric structure to produce an equally thermostable polymer. Keller and co-workers reported the synthesis and polymerisation of phthalocyanine resin using molecular chains end-capped with PN units that exhibited attributes for advanced structural applications. They attempted diverse backbone structures for the design of versatile PN systems [1–12]. Majority of the research related to PN systems are focused on two areas: (1) design and synthesis of PN-based monomers/oligomers containing a variety of linkages and groups and (2) investigations on a variety of curing agents to cut short their tedious cure schedule.
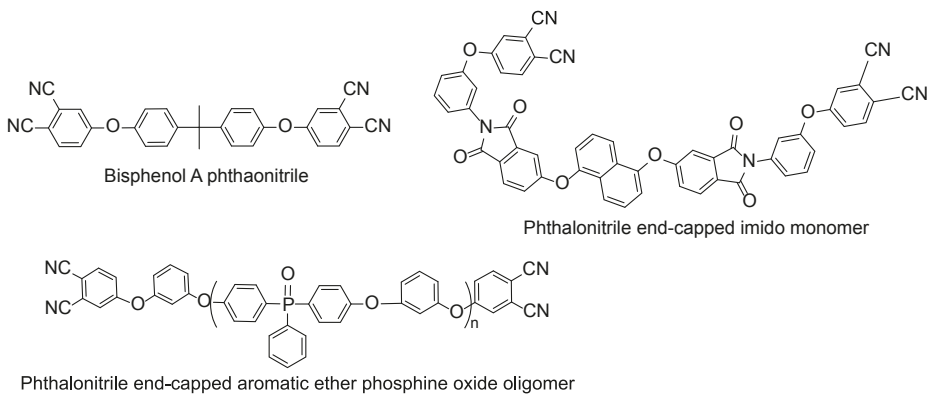
PN polymers are formed from monomers or oligomers containing PN groups either at chain ends or along the backbone. The spacers between terminal PN units can be vinyl ester networks, bisphenols, aromatic ether phosphine oxide, polybenzoxazines, imides and so on. Chemical structures of some of the PN monomers/oligomers are shown in Scheme 2.1.

PN monomers/oligomers are generally synthesised by the nucleophilic displacement of nitro group in nitro PN by the free phenolic fractions in the starting material in an alkaline medium (Scheme 2.2). Commonly used solvents are dipolar aprotic solvents such as *N*-methyl pyrrolidone, dimethylformamide, dimethylacetamide and so on. These solvents enable the reactants to go into the solution much faster and augment the reaction rate. An alternative method involving the condensation of bisphenols with dibromobenzene using K_2CO_3 as the base and $(PPh_3)_3CuBr$ as the catalyst is also reported, which is very feasible for realising multiple aromatic ether-linked PN oligomers [13]. In recent years, a greener approach to polymerisation reactions is gaining wide attention. Eco-friendly routes such as the use of ionic liquids (IL) as the polymerisation media and microwave (MW) as the heating source have been explored [14, 15]. IL readily absorb MW energy and can be heated rapidly due to its high polarity and electrical conductivity. In this line, synthesis of imide-containing PN monomers in

1-butyl-3-methyl imidazolium chloride as IL media along with MW was investigated, which showed that the reaction time can be reduced to 13 min with increase in yield [16].

Bisphenol A phthaonitrile

Phthalonitrile end-capped imido monomer

Phthalonitrile end-capped aromatic ether phosphine oxide oligomer

Scheme 2.1: The structure of various PN monomers and oligomers (BPhAPN: bisphenol A phthalonitrile).

R = any linking group
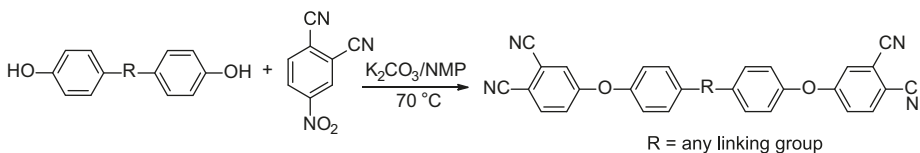
Scheme 2.2: General protocol for the synthesis of PN monomers (NMP: *N*-methyl-2-pyrrolidone).

Depending on the structure of the prepolymer, the resins may be extremely slow in curing to the polymeric state. A typical procedure to get a prepolymer is to melt the monomer in the presence of a curing agent and quench the product to room temperature (RT). This B-stage resin can be stored for an indefinite period under ambient conditions without any further reaction [17, 18]. The polymerisation occurs above the melting point or glass transition temperature and can be controlled as a function of quantity of curative and curing temperatures.

2.3 Cross-linking of PN groups

Uncatalysed polymerisation of PN resin is extremely difficult because of the lack of active hydrogen and rigidity of the linking sites that hinder the accessibility of the reactive sites. This warrants extended durations and elevated temperature for

the gelation to occur. It is not always possible to increase the temperature to accelerate the cure rate because the prepolymer may volatilise or decompose before polymerisation gets initiated. Further, the higher temperatures result in a less practical processing environment. A small quantity of curing agent is known to induce cure reaction of nitrile groups and the thermal polymerisation rate can be controlled as a function of concentration of these additives and curing temperatures [12, 19, 20]. Generally, a hydrogen source such as amine or hydroxyl groups is needed as cure promoters. Different cure conditions have been reported in literature starting from 260 °C to a post-cure temperature of 375 °C for 24 h in nitrogen atmosphere [21].

2.4 Cure accelerators

PN prepolymers follow an addition cure mechanism to form highly cross-linked heterocyclic polymer networks without the evolution of volatile by-products. The polymerisation reaction propagates through multiple reaction pathways, forming highly aromatic heterocyclic intermediates such as polytriazine, polyimine and polyphthalocyanine (Scheme 2.3), which is conducive for the high thermal and oxidative stability and mechanical properties [22]. Small quantity of catalysts such as amines and phenolic to the tune of 1–2 wt% of monomer is added to the resin to promote the cross-linking [23, 24]. The overall cured network structures depend on the type and quantity of cross-linking agent. The
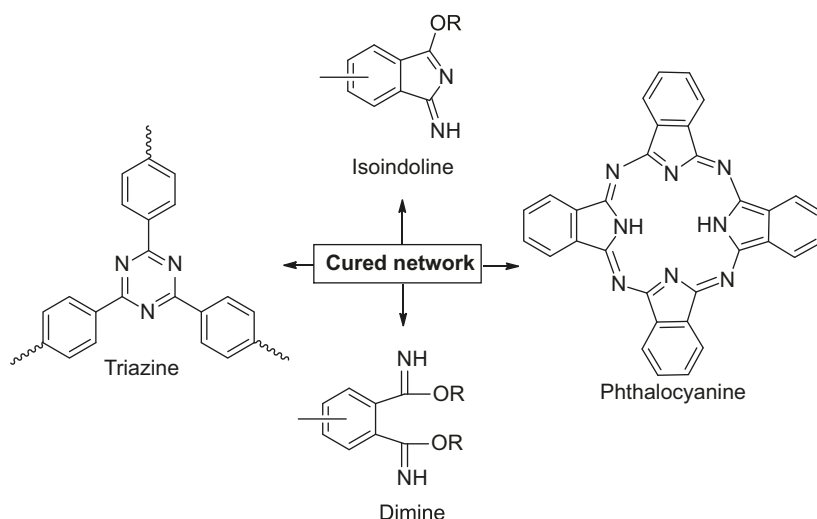

Scheme 2.3: Probable reaction products of PN polymerisation.

formation of intermediates is confirmed mainly from spectroscopic techniques. Weak absorptions at 1,563 and 1,325 cm^{-1} in Fourier-transform infrared (FTIR) are characteristics of triazine network and absorption at 1,010 cm^{-1} to phthalocyanines. FTIR absorptions at 1,600 cm^{-1} (C=N) and 3,300 cm^{-1} (N–H) indicate isoindoline structures. The peak at 1,720 cm^{-1} is also attributable to the characteristic absorption of isoindoline ring. In ^{1}H-nuclear magnetic resonance, the protons resonating between 9 and 9.3 ppm are characteristic of N–H protons, which can be attributed to isoindoline-type protons. Peaks at upfield chemical shifts between –8 and –9 ppm are indicative of phthalocyanines and a sharp doublet at 9 ppm is characteristic of triazine rings [25, 26]. In ultraviolet–visible spectrum, PN networks give two strong absorption bands: the one at 290–380 nm region corresponds to B-band due to isoindoline structures and the second band at 620–750 nm (a Q-band) to the phthalocyanines [27].

Some of the cure promoters that are generally used for the PN systems are described in Sections 2.4.1–2.4.6.

2.4.1 Metal salts and complexes

The hydrogen source as curatives can pose problems as they can partially volatilise during vacuum degassing of the resin and thus change the cure rate and polymer properties. Alternatively, metal ions can be used to accelerate the polymerisation of PN. The most common form of bonding between nitriles and metal ions is thought to be linear with the metal centre coordinated to the nitrogen lone pair, resulting in polarisation of the carbon–nitrogen bond and leads to significant activation of the bond toward nucleophilic addition. The commonly preferred metals are copper, iron, zinc and nickel. Other metals like molybdenum, vanadium, beryllium, silver, mercury, tin, lead, antimony, calcium, barium, manganese, magnesium, cobalt, palladium and platinum are also employed. Metallic salts including stannous chloride, cuprous bromide, cuprous cyanide, cuprous ferricyanide, zinc chloride, zinc ferrocyanide, ferrous chloride, ferrous ferricyanide and so on are also explored as curing agents [28, 29]. The PN resins produced by this method are not as thermally stable as is required for many applications and there are processing problems associated with the method such as requirement of large quantity of metals or metal salts for achieving complete reaction. Because of the higher density of the metals compared to the resin, the metals settle out when the resin melts and thus give non-uniform cures and materials. A recent report suggests ammonium molybdate tetrahydrate/urea mixture as a plausible curing agent for PN resins [30]. Walton patented the use of ionic metal phthalocyanines as efficient cure accelerators as the solubility of these complexes in different solvents ensure homogeneous polymerisation [28]. Scheme 2.4 shows phthalocyanine network formation of PN in the presence of metal.
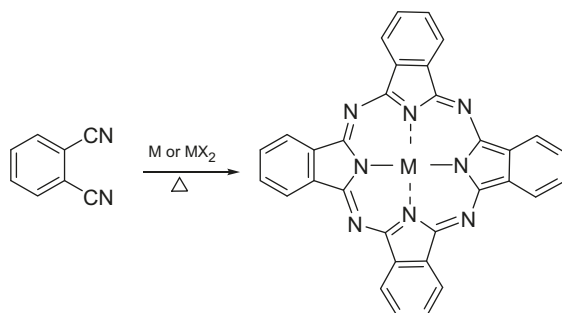
Scheme 2.4: Curing of PN using metals (M)/metal salts (MX$^{2)}$·

2.4.2 Phenols

Commonly used phenols are bisphenol A (BPA), bisphenol S, bisphenol A6F, resorcinol, hydroquinone, 4,4′-dihydroxy biphenyl and BPA polysulfone [11]. Phenolic groups trigger the cyclisation reaction through the formation of iminoesters that can undergo further reaction intermolecularly with other nitrile functionalities to give triazine networks. Participation of the iminoester in an intramolecular reaction with a nitrile group leads to the formation of isoindolines. The isoindoline may further react with PN to form a tetrameric phthalocyanine groups [31, 32].

Mechanism of phenol-accelerated nitrile cure reaction is depicted in Scheme 2.5.

2.4.3 Amines

Even though all amines promote the nitrile cure reactions, primary aromatic amines are found to be more effective. Aliphatic amines are usually excluded from this selection as they are easily decomposable and may affect the integrity of structural components [33, 34, 35]. The amine groups attack the nitrile functions in PN moieties to form amidine intermediates [36]. The imine linkages in the amidine undergo an intramolecular attack with the nitrile group, leading to the formation of isoindoline structures. The isoindolines can further react with other PN end-capping units to form PN networks [25]. Amidines can also proceed through an intermolecular reaction with other nitrile functionalities to form triazine rings [26, 37]. Mechanism of amine-mediated PN curing is shown in Scheme 2.6.

The commonly used amine curing agents include primary or secondary amines like *meta*- and *para*-phenylenediamine, aminophenyl ether, 4,4′-diaminodiphenyl ether, methylene dianiline, aminophenylsulfone and 1,3-*bis*(3-aminophenoxy)benzene (APB) [17, 19]. Chemical structures of some of these amine curing agents are shown in Scheme 2.7. The studies done at Naval Research Laboratory have shown
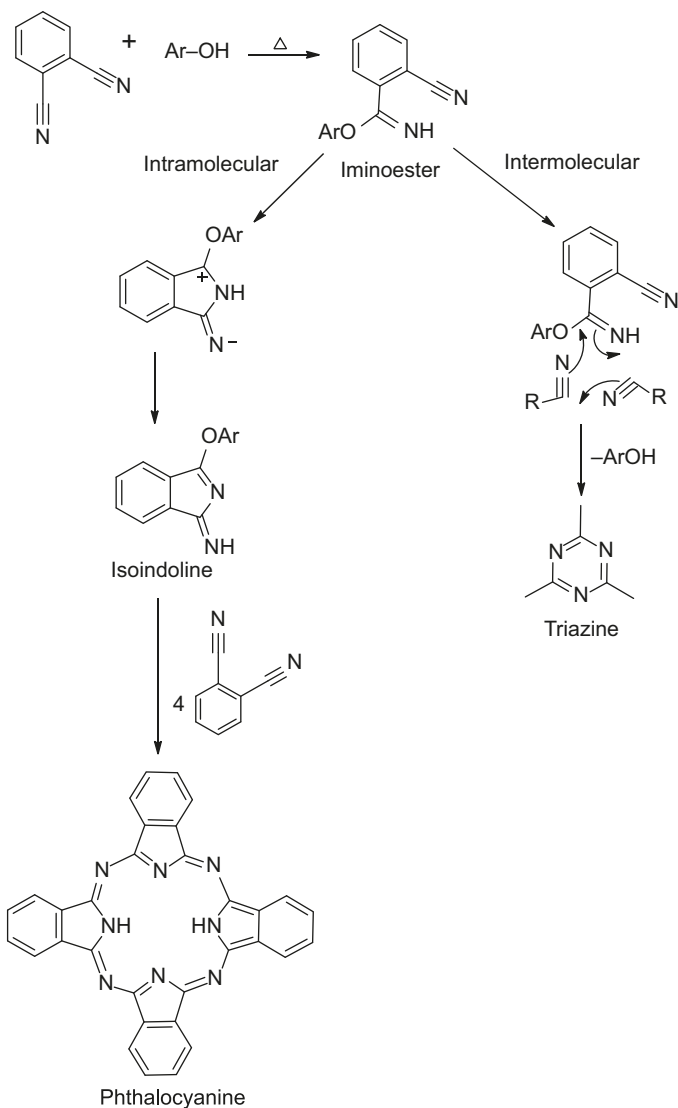
Scheme 2.5: Probable mechanism of phenol-mediated PN curing. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *European Polymer Journal*, 2015, 71, 389. ©2015, Elsevier [38].

that the use of aromatic amines as curing agent raises the problem of volatility and may affect the processability of the resin, which can be overcome to a large extent by employing high molecular weight, sulfone-containing amines such as derivatives *meta-bis*[(aminophenoxy)phenyl]sulfone (*m*-BAPS) or *para-bis*[(aminophenoxy)phenyl]sulfone (*p*-BAPS) [38]. Simple amine-functionalised PN molecule as a curing agent instead of diamines can further enhance the cross-linking density and can
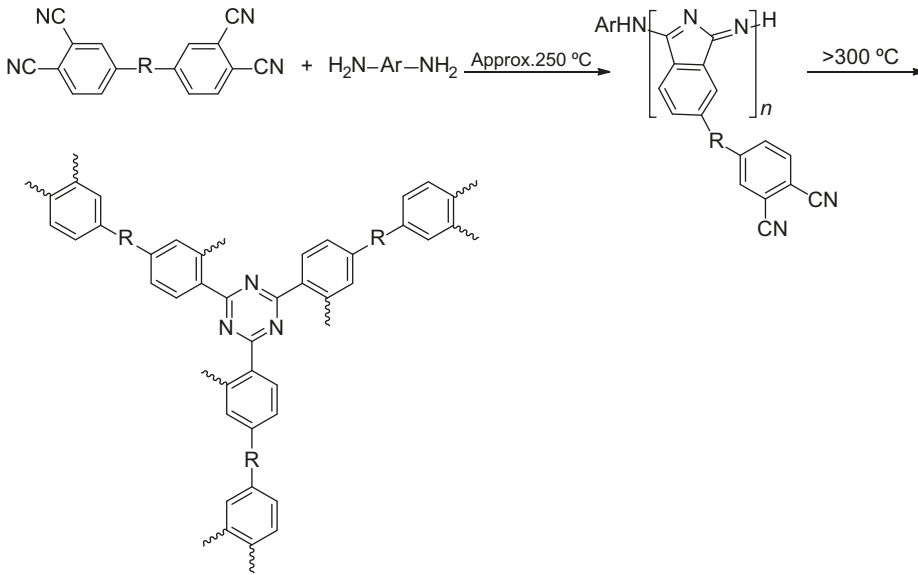
Scheme 2.6: Amine-catalysed curing of diphthalonitrile monomer.
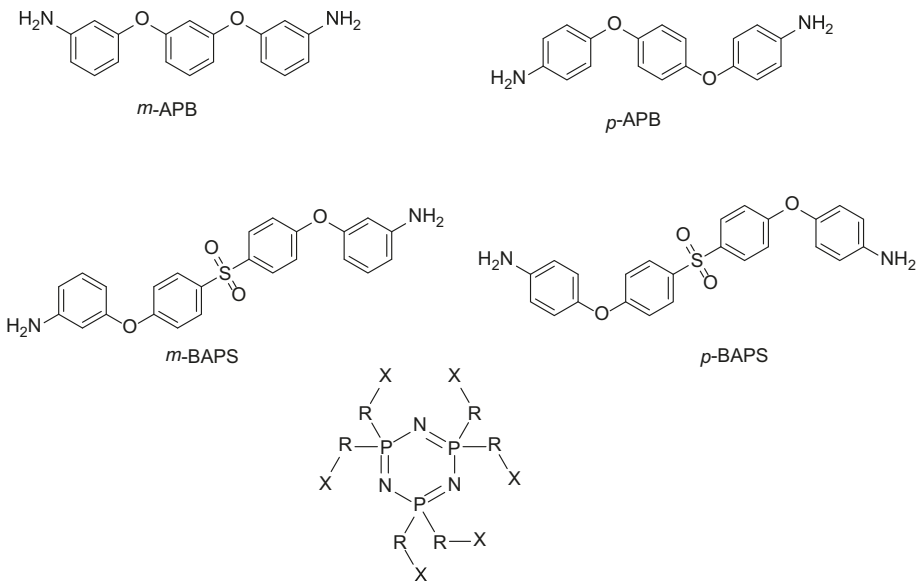
Scheme 2.7: Preferred amine curatives for PN resins (R: alkyl, aromatic, alkyl-substituted aromatic groups; and X: amine groups).

improve the thermal and thermo-oxidative properties of cured networks [39]. Alkaline earth salts can function as Lewis acid-type catalysts and activate C≡N bond towards the nucleophilic addition of a primary aromatic amines to PN [40].

Linear phosphazene or cyclic phosphazene-containing amines are reported to induce polymerisation of the nitrile functions. The curing agents based on phosphazenes (*bis*-, *tris*- and tetrakis-maleimidophenoxy-triphenoxy cyclotriphosphazene resins) enhance the rate of cure and also add flame retardancy to the cured polymers [41, 42]. A general representation of phosphazene curing agent is shown in Scheme 2.7.

2.4.4 Acids

Acids that are proton donors or electron acceptors can be used as a nitrile cross-linking agent. During acid-catalysed polymerisation, the reaction occurs by an electrophilic attack of the acid group on the cyano units of the PN monomer or prepolymers. Strong inorganic acids, typically mineral acids, are not preferred because of their high oxidation strength. Organic acids including *p*-toluenesulfonic acid, aniline-2-sulfonic acid, 8-aniline-1-naphthalenesulfonic acid, 4-aminophenylphosphonic acid and so on, and Lewis acids of aluminium and boron compounds can also be used. These curing agents are especially useful for the highly aromatic PN monomers whose melting points are above 200 °C [43, 44].

2.4.5 Self-catalysed PN resins

Usually, the PN monomers are of high melting points (>200 °C) and for developing their binary PN/curative composition, extreme conditions are required. The monomer should be melted over 230 °C prior to the addition of aromatic amines and then mixed vigorously. Therefore, the development of a self-catalysed PN monomer with low melting temperature would be interesting in view of science and industrial applications. This discussion is elaborated in Chapter 4.

2.4.6 MW-assisted curing of PNs

Polymerisation of PN resins necessitates very high temperatures and several hours of reaction time. Duration of cure reactions though could be reduced by using curatives, post-cured networks still contain uncured nitrile groups. This may be due to the inappropriate heat transfer to the reactant molecules [45, 46]. Hence, it is necessary to explore approaches to increase the processability and decrease the polymerisation reaction time with an efficient alternative heating. Some researchers have

utilised MW technology for curing of PN-based systems. Compared to the conventional heating process, it gives advantages like fast processing, high yield and reduced side reactions [47, 48]. The feasibility of curing naphthalene-based PN monomer containing imide linkage under MW irradiation was explored, wherein the reaction time was significantly reduced from several hours to nearly 1 h, with complete consumption of nitrile groups [49]. FTIR analysis of MW-cured imide linkage containing PN resin with 3 wt% of oxy dianiline (ODA) as a curing agent showed that polymerisation was achieved in couple of hours [50].

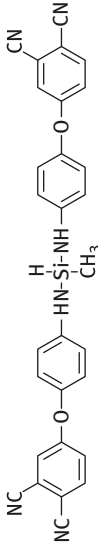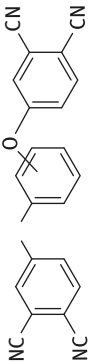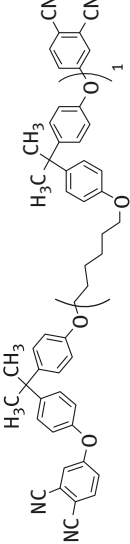Thermal properties of some PN monomer/curative compositions are compiled in Table 2.1.
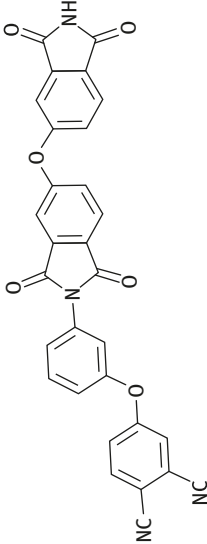
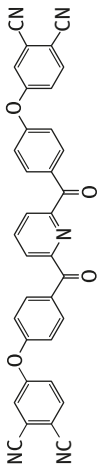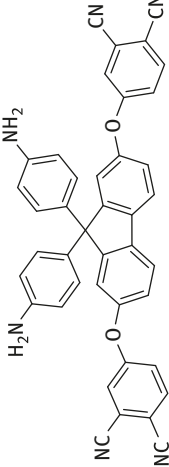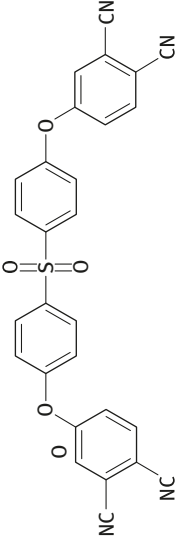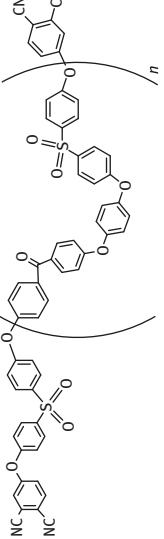## 2.5 Comparison with other high-performance matrices and composites

Modern structures of aerospace vehicles demand polymeric materials with outstanding thermal stability to withstand extreme temperature conditions. The major difficulties encountered by the majority of high-temperature polymers include poor processability and evolution of volatile products on curing. It has been found that the incorporation of aromatic and heterocyclic segments into the polymer network makes them thermally stable. However, this approach often makes the system brittle and impedes processability. Currently, high-performance structural components are mainly moulded from epoxies and polyimides (PI) with structural variations. Nonetheless, they are not free from drawbacks and cannot be pushed as ideal threshold materials for most of the advanced applications. Conventional epoxy-based composites and adhesives have 200 °C as maximum service temperature limit and PI resins used in composites matrices have 300 °C as maximum service temperature. Advanced design concepts, especially in the aerospace industry, demand even higher temperature requirements for polymeric materials. PI system, though apt in terms of temperature performance, suffers from inability to process void- and blister-free components as evolution of volatile components occur during their polymerisation. Major concerns associated with both PI and epoxies include their brittleness, water absorptivity and engineering non-reliability.

Interest in fibre-reinforced composites for advanced aerospace applications has led to the search for high-temperature polymers that are easily processed and exhibit high thermal and oxidative stability. Research studies on PN resins suggested that they can be a potential candidate in future endeavours. Foremost, addition cure mechanism of PN systems ensures that little or no volatiles are evolved during the polymerisation, leading to highly cross-linked, void-free network polymers having good mechanical properties, outstanding thermo-oxidative stability at elevated temperatures, superior fire resistance relative to other conventional polymers and low water absorptivity. Excellent mechanical and thermomechanical properties in conjunction with their processability into void-free composites make PN polymers
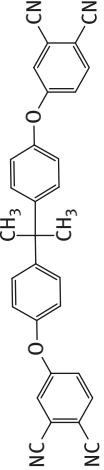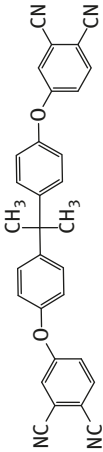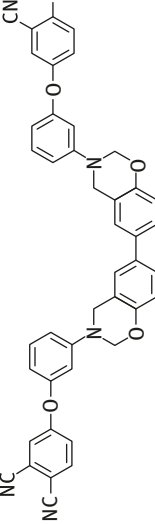
Table 2.1: Some PN monomers and their curing agents.

Monomers/oligomers structure		Curing agent	Cure exotherm peak temperature (°C)	5% Mass loss temperature (°C) (N$_2$)	Char residue (%) (N$_2$)
(structure)	Phthaloimido PN	Nil	–	517.7	69 (800 °C)
(structure)	Silicon-containing PN	Nil	255	570	83 (1,000 °C)
(structure)	Dihydroxy benzene PN	ODA	o = 246 m = 254 p = 257	o = 461 m = 485 p = 422	o = 68 m = 69 (1,000 °C) p = 57
(structure)	Aliphatic-aromatic ether PN	*m*-BAPS	255	430	52 (1,000 °C)

Pyridine-containing PN	4-(Aminophenoxy) phthalonitrile	244	521	71 (1,000 °C)	
Amine-containing fluorene PN	Nil	245	513	76 (800 °C)	
Bis[4-(3,4-dicyanophenoxy)phenyl]sulfone	APB	259	418	59 (1,000 °C)	
Sulfone-ketone PN	m-BAPS	235	480	60 (1,000 °C)	

(continued)

Table 2.1 (continued)

Monomers/oligomers structure	Curing agent	Cure exotherm peak temperature (°C)	5% Mass loss temperature (°C) (N_2)	Char residue (%) (N_2)
BPhAPN	Nil	–	410	8 (900 °C)
BPhAPN	APB	270	~480	60 (1,000 °C)
Bisphthalonitrile-containing benzoxazine units	Nil	230, 275	478	76 (800 °C)

m: meta;
o: ortho; *p*: para.

superior to the state-of-the-art high-temperature polymers such as polymerisation of monomeric reactant (PMR)-15. Table 2.2 compares the mechanical properties of PN, PMR-15 and a cyclic aliphatic epoxy neat resin at RT [51, 52]. Mechanical characteristics of PN neat resins were either superior or comparable to the other thermosets.

Table 2.2: Mechanical properties of neat resins at RT.

Property	PN	PMR-15	Cyclo aliphatic epoxy
Tensile strength (MPa)	85	43–80	89
Tensile modulus (GPa)	4.4	4	6.3
Elongation at break (%)	1.2	1.4–2.5	2.1
Flexural strength (MPa)	80	76	159
Flexural modulus (GPa)	4.2	3.2	6.4
Fracture energy (J/m^2)	120–130	87	–
T_g (°C)	>450	330	–
Upper-usage temperature (°C)	>371	288	–
Water uptake (% in 2 weeks)	0.6	1.6	–

For PN, flow conditions are maintained by controlling polymerisation rates as functions of amount of curing additives and temperature. Therefore, their composites can be fabricated using conventional autoclave curing and also by automated procedures like resin infusion moulding, resin transfer moulding and filament winding [53]. Table 2.3 compares the RT mechanical properties of Hexcel® IM7 carbon fibre-reinforced composites of PMR-15 and PN systems. Mechanical properties of PN composites are found to be comparable or superior to PMR-15-based composites [18, 54–57].

Table 2.3: Mechanical properties of PMR-15 and PN composites.

Property	PN-Hexcel® IM7	PMR-15 Hexcel® IM7
0° tension:		
Strength (MPa)	2,000 ± 20	2,500 ± 175
Modulus (GPa)	183 ± 3.7	146 ± 4.4
Strain (%)	1.0 ± 0.0.7	1.6 ± 0.06
0° flexure:		
Strength (MPa)	2,350 ± 47	1,530 ± 76.5
Modulus (GPa)	174 ± 3.5	122 ± 4.9
Strain (%)	1.3 ± 0.23	1.3 ± 0.08
Short beam shear strength (MPa)	85 ± 1.7	105 ± 2.1

Adapted from B.D. Sartwell, *AMPTIAC Newsletter*, 1999, 3, 3, 12 [56].

A comparative study of the thermal stabilities of PN composite systems with corresponding composites of various high-performance matrix resins showed that PN exhibit thermal degradation onset temperature around 500 °C with char yield >70% in majority of the PN polymers explored so far. Graphite–PN composites show retention in their tensile strength up to temperatures close to 538 °C for short exposure times (~400 s), while the graphite–epoxy systems that are used as a major component in missile and aircraft structures show a rapid decline in their tensile strength at 260 °C. This shows the potential of PN resin systems in thermo-structural applications [58].
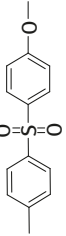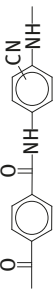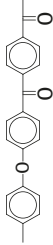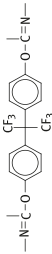
The fire performances of PN composites are much superior to the other organic polymer composites. They are the only materials that meet the flammability requirements of MIL-STD-2031 standard for use of polymeric composites aboard navy submarines [52, 57–59]. The excellent ignition resistance of these materials is attributed to several factors including their high thermal stability and low release of flammable volatiles as well as formation of large amount of char during decomposition [52]. Table 2.4 lists the flammability characteristics of typical thermosetting polymers and their glass fibre-reinforced composites [51]. The time to ignition for PN is about 30% more than for bismaleimide (BMI) or epoxy systems. In addition, the PN system exhibit significantly lower heat generation than other polymer composites.

Table 2.4: Flammability characteristics of glass fibre-reinforced composites based on PN and other thermosetting polymers (as evaluated per MIL-STD 2031 standard).

Matrix resin	Peak heat release rate (100 kW/m^2)	Ignition time (s)	
		Heat flux (50 kW/m^2)	Heat flux (100 kW/m^2)
MIL-STD 2031	150	150	60
Epoxy	232	105	40
Bismaleimide	285	141	38
Phenolic	133	No ignition	25
Polyimide	85	No ignition	55
PN	106	No ignition	59
Vinyl ester	187	67	24
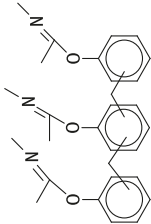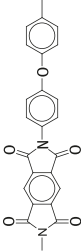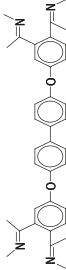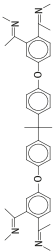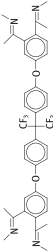
The optical density and relative amounts of toxic gases (CO, HCN and HCl) are significantly lower for PN/glass composites. For instance, the amount of CO generated from PN/glass composite is 40 ppm, while the CO emission in other glass-reinforced composites are PI (200 ppm), phenolic (300 ppm), BMI (300 ppm), epoxy (280 ppm) and vinyl ester (230 ppm). PN/carbon composites exhibit low water uptake, that is, <1% after exposure to water for 16 months [59]. These combinations of attractive attributes make PN systems promising candidate for high-performance composites in aerospace and advanced military and marine applications.

Table 2.5: Thermal and flame resistance of PNs vis-à-vis classical polymer systems [59].

Material	Repeat unit structure	Heat release capacity (J/gK)	Total heat release (kJ/)	Char (%)
Poly(1,4-phenylene ether sulphone) (PES)		115	11.2	29.3
Cyano-substituted Kevlar		54	9.1	58.3
Poly(ether ketone ketone)		96	8.7	60.7
Polybenzimidazole(PBI)		36	8.6	67.5
Hexafluorobisphenol A polycyanurate		32	2.3	55
Bisphenol A epoxy, catalytic cure		657	26	3.9

(continued)

Table 2.5 (continued)

Material	Repeat unit structure	Heat release capacity (J/gK)	Total heat release (kJ/)	Char (%)
Novolac polycyanurate		122	9.9	51.9
Polyimide (PI)		25	6.6	51.9
Biphenol phthalonitrile		15	3.5	78.8
Bisphenol A phthalonitrile		40	5.9	73.6
Bisphenol A6F phthalonitrile		9	2.8	63.8

Molar group contributions to polymer flammability calculated from additive molar group contributions based on the chemical structure of the polymers are given in Table 2.5 [60]. It can be seen that in contrast to the state-of-the-art high-temperature-resistant thermosets and thermoplastics, PN polymers have a very low heat release capacity and total heat release capacity.

PN resins too are not devoid of limitations. The higher melting point, usually greater than 200 °C, is a common shortcoming in PN monomers [2, 9, 61, 62]. For example, the melting point of the biphenyl PN monomer is 230 °C with a narrow processing window (the gap between the melting point and the polymerisation temperature) of only 20 °C on using amine curatives, which causes difficulties in processing and hampers its wide applicability [17]. Therefore, there is growing interest in two research directions for the development of new PN-based polymers and they are generally classified into (1) the utility of various curing additives, which is expected to initiate the curing process and shorten the curing time of the PN and (2) PN-based monomers/oligomers containing a variety of linkages and groups, which can be designed and synthesised to pursue low melt viscosity and broad processing window for these systems for advanced applications.

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3 Structure–property relationships

3.1 Introduction

Over the past decade there has been much interest in improving the mechanical properties, solvent resistance and thermo-oxidative stability of thermoset polymers for advanced applications. Development of novel phthalonitrile (PN) systems that exhibit excellent thermomechanical performance to expand their end-use applications in severe environments is a big challenge. End-capping of the polymers with functional groups that cure into highly cross-linked, high glass transition temperature (T_g) networks at temperatures greater than 200 °C has been identified as a favourable method to produce polymers with high thermo-oxidative stability. The use of high-temperature performing functional groups allows for retaining the processability of these polymers, while producing a highly cross-linked network having increased levels of aromatic and heterocyclic ring structures within the network [1].
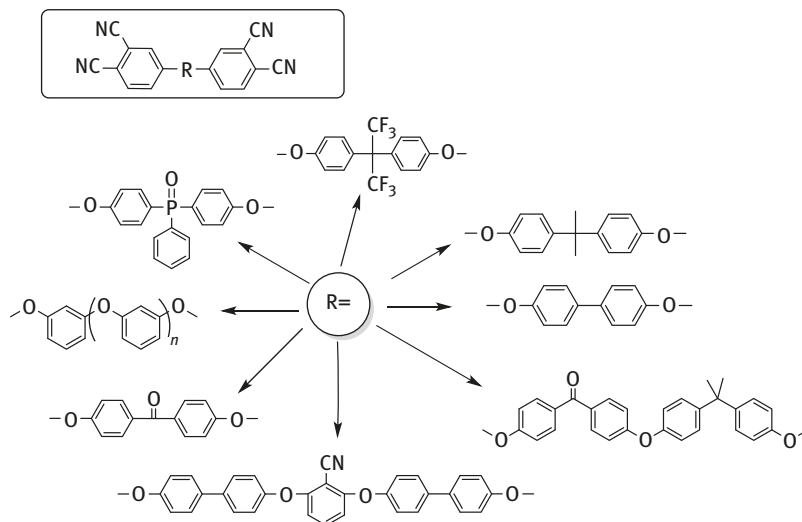
The research on development of PN polymers flourished with the advent of studies on PN systems with various backbones by Keller and his team from 1980 onwards. These resins were derived by heating the PN monomers in the presence of a small amount of curing additives for extended periods of time at elevated temperatures. Thereafter, a lot of studies have been directed towards the chemical structural modifications in PN polymers in order to fine-tune their properties. As a result, a plurality of bisphthalonitrile monomers containing aromatic ether, thioether, imide, sulfone and other linkages between the terminal PN units have been synthesised by other researchers (Scheme 3.1) [2].

This chapter gives an account of the structure–property relationship of various PNs that have been reported and the chemical modification approaches for PN polymers. The systems have been broadly classified into (i) fluorine-functionalised PN, (ii) imide-functionalised PN, (iii) benzoxazine-functional PN, (iv) polymer backbone bearing ether, sulfone, phosphine oxide, allyl and amide moieties, bioderived PN polymers and (v) conducting PN polymers. The dependency of their properties on structural features is also examined.
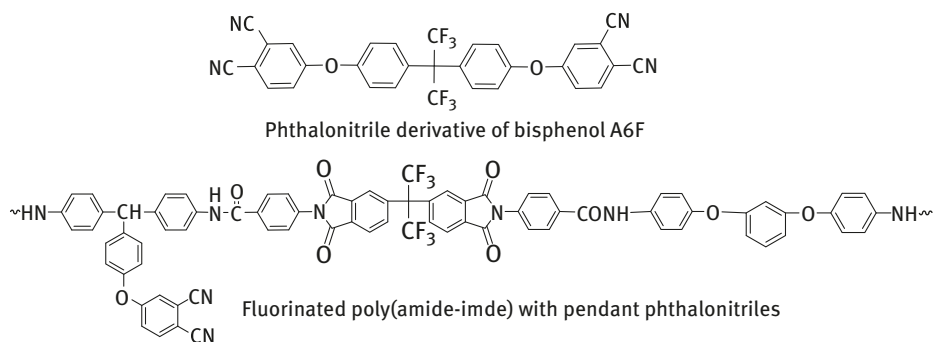
3.2 Fluorine-containing PNs

It is well known that fluorine groups have the capability to alter the physical/physicochemical properties such as chemical stability, melting point, flammability and solubility of a compound. Based on this idea, some researchers tried to incorporate fluorine chemistry into the PN monomeric structures for acquiring many desirable features. Presence of fluorocarbon bridging chains imparted water repellency and oxidation resistance to the PN networks (Scheme 3.2). Polyphthalocyanine resin systems

Scheme 3.1: PN monomers containing various backbones [2].

Phthalonitrile derivative of bisphenol A6F

Fluorinated poly(amide-imde) with pendant phthalonitriles

Scheme 3.2: PN having fluorocarbon bridging chains.

from perfluorinated aliphatic phenoxy bisorthodinitrile exhibited high service temperature (300 °C) with extremely low surface energy, very low water absorptivity and high resistance to acids [3]. However, in one of the studies, it was shown that the high fluorine content disfavoured the phthalocyanine formation and instead led to the nucleophilic displacement of fluorine by the cyano-functionalities themselves [4, 5]. As an alternative route, the synthesis of fluorocarbon PN by copper-catalysed reactions involving substitution and iodo-coupling reactions is more dependable [6, 7].

Fluorinated polyamide-imides with PN groups have found use as actuators and exhibited high thermal stability with initial decomposition temperature above 420 °C [8]. They were highly soluble in polar aprotic solvents due to the hindrance to close

packing of polymer chains by the six fluorine groups. The amount of PN groups influenced their electrical and nanoactuation properties. The dielectric permittivities of polymer films measured at 10 kHz at 20 °C were in the range of 3.01–3.43, and nanoactuation in the range of 120–450 nm at 220 V direct current [9].

In bisphenol-based PN, polymer based on 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane (6FPh) showed high oxidative stability when compared to their non-fluorine-containing counterparts [4,4′-bis(3,4-dicyanophenoxy)biphenyl (BPhPN) and 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]propane (BPhAPN)] [10, 11]. When these polymers are polymerised in the presence of an amine catalyst, the fluorine-containing monomer with the electron-withdrawing O=C–(CF$_3$)$_2$O linkage was more susceptible to a nucleophilic attack by the diamine relative to the BPhAPN monomer. The rate of polymerisation followed the order: 6FPh > BPhPN > BPhAPN. This is because the nitrile groups in the 6FPh monomer are more electrophilic due to the presence of electron-withdrawing OC(CF$_3$)$_2$O linking unit relative to O=C(CH$_3$)$_2$O linking group in BPhAPN monomer.

3.3 PNs with imide functionalities

Owing to their desirable thermal and thermo-oxidative stability and electrical properties, polyimides (PI) are well known as composite matrices for a variety of applications. However, the highly rigid aromatic backbone content makes them difficult to be fabricated into useful end products and they are not free from voids either. To solve these issues, it is desirable to end-cap the imidised polymers with cross-linkable reactive sites. Many studies adopted the approach of incorporation of PN sites to PI backbone and all of them were successful in yielding void-free materials with enhanced thermo-oxidative stability [12–16]. A general route for the synthesis of PN resin with imide and ether linkages includes the reaction of an aminophenoxy PN with an aromatic dianhydride followed by chemical/thermal imidisation (Scheme 3.3). The formation of intermediate amic acid was confirmed from the coupling constants for *ortho*-coupled protons of dianhydride and PN parts. These polymer networks were found to be thermally more stable than the epoxies, bismaleimides (BMI) and other conventional thermosetting PI.

The synthesis time for this polymer was short and resulted in high yield. Since the imide linkages in the interconnecting units between the terminal PN are formed before the polymerisation occurs, void-free components could be fabricated. Also, the thermal stability of these classes of polymers was superior when compared to the general bisphenol-based PN. Achar and co-workers reported the transformation of the imide-linked bisphthalonitrile monomers to the cured networks of phthalocyanine by simply heating or in the presence of a metal powder. This resulted in products with enhanced fire resistance, toughness and moisture resistance [17, 18] (Scheme 3.4). For poly(copper phthalocyanine)imides, the initial decomposition
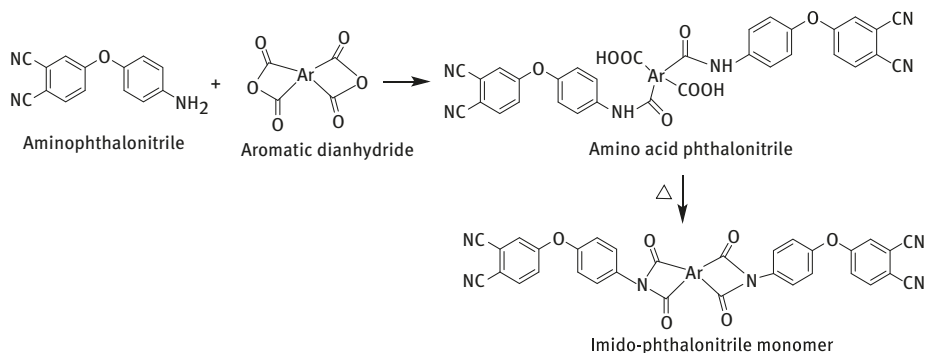
**Scheme 3.3:** Synthesis of imide-funtionalised PN.
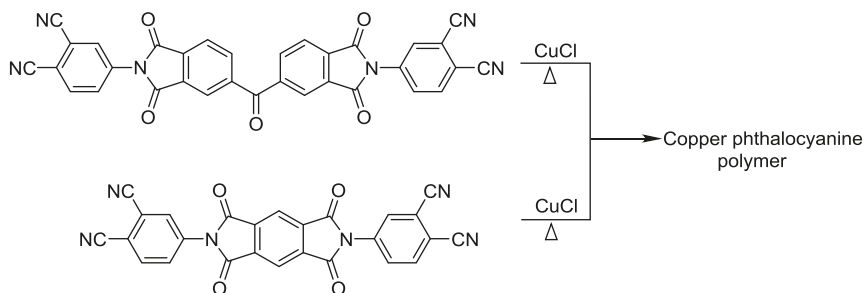
Scheme 3.4: Polymerisation of imide-containing PN monomers in the presence of metallic salt.

temperatures were in the range of 420–470 °C (in air), around at 580 °C (in N_2) and a whooping anaerobic char yield of 73–76% at 800 °C [19].

Incorporation of fluorene, phthalazinone and ester-imide linkages confers many desirable properties to the resin [10, 11, 17, 20, 21]. Three polymerisable bisphthaloni-trile monomers, BHF–PN, BHMF–PN and BHA–PN (Scheme 3.5), are reported by Achar and co-workers, which can be formed from the reaction of 4-nitrophthalonitrile with 9,9-bis(4-hydroxyphenyl)fluorene, 9,9-bis(3,5dimethyl-4-hydroxyphenyl)fluo-rene and phenolphthalein [11]. Thermal stability of the compounds follows the order: BHA–PN > BHF–PN > BHMF–PN. Presence of fluorene moiety and phthalic anhydride group in these compounds conferred very high thermal stability and fire resistance to their polymers.

For realising PN with ester-imide linkages, initially bisphthalic anhydrides were synthesised by the reaction of hydroquinone or 4,4′-thiodiphenol with trimel-litic anhydride acid chloride in the presence of pyridine. Bisphthalic anhydrides were further made to react with 4-aminophthalonitrile (4-AmPN) to give bisphthalo-nitrile derivatives with ester-imide linking groups. Their copper halide–catalysed polymers showed char yield of 50% at 800 °C. For a proper control over the
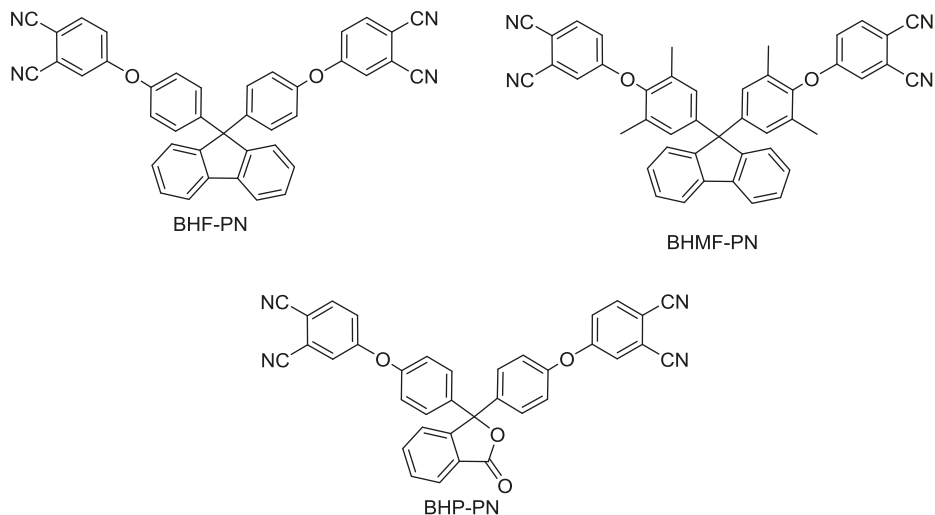
Scheme 3.5: Polymerisable bisphthalonitrile monomers.

flexibility and rigidity of thermosets, it is an effective approach to incorporate ether units and heterocyclic rings to the monomeric structure. In this aspect, a two-step, one-pot reaction was employed for synthesising soluble and curable PN-terminated oligomeric polyetherimides (PEI)-containing phthalazinone moiety from an excess amount of three dianhydrides and phthalazinone-based diamine, followed by reacting with 4-(3′-aminophenoxy)phthalonitrile (4-3′APPN) [20]. The incorporation of phthalazinone into the polymer chain results in an improvement in the solubility and T_g. These oligomers showed high T_g in the range of 214–256 °C and high decomposition temperatures with 10% weight loss ($T_{10\%}$) ranging from 523 to 553 °C. The cross-linked polymers were insoluble in all solvents and did not exhibit a T_g up to 350 °C and their $T_{10\%}$ was in the range of 543–595 °C.

A two-step process was employed to realise phosphorus-containing polyester-imide having pendant PN groups [21]. In the first step, the polyamic acid was prepared by the reaction of the aromatic diamine bearing a PN group with phosphorus-containing dianhydride at room temperature (RT) (Scheme 3.6). This was followed by cyclo-dehydration of polyamic acid to the corresponding imide structure in the presence of a mixture of acetic anhydride/pyridine. The polymer was soluble in aprotic polar solvents such as N-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc) and dimethylformamide (DMF), ascribed to the presence of bulky phosphorus units such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) with polar P=O group. Pendant DOPO and PN units imparted disorder in polymer chains and hindered the dense chain stacking, thereby reducing the interchain interactions and thus improving solubility. T_g of cured polymer was around 252 °C and it began to decompose in the range of 367–408 °C. It exhibited a two-stage decomposition pattern: first, due to
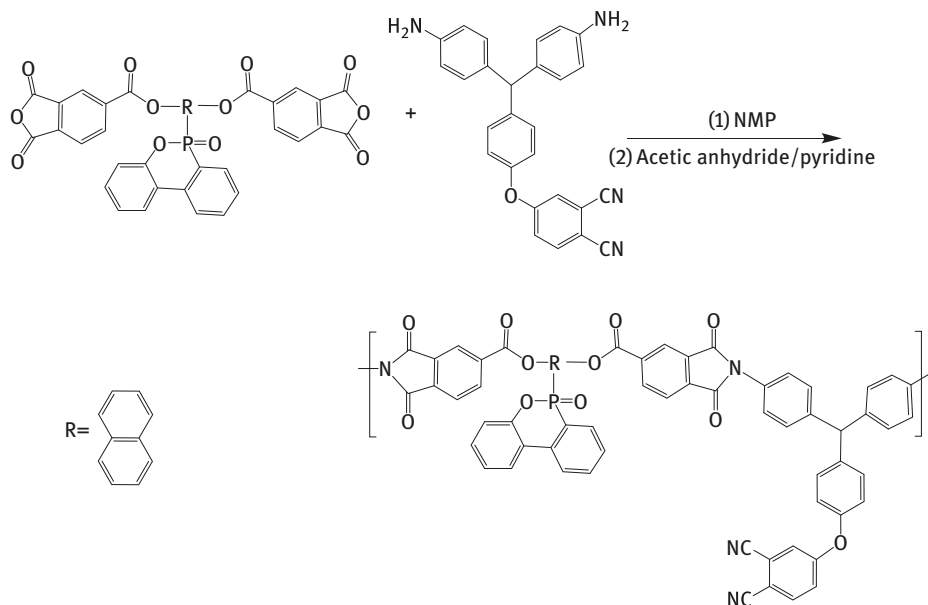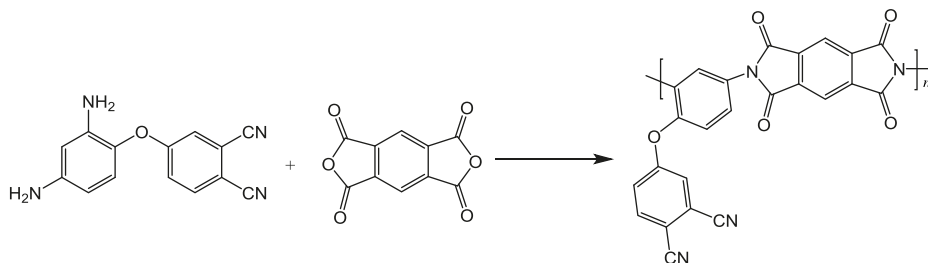
Scheme 3.6: Preparation of phosphorus-containing polyester-imide having pendant PN groups.

decomposition of sensitive ester and DOPO units and second due to decomposition of polymer chain itself. Fourier transform infrared (FTIR) spectrum of solid residue after the first destruction stage showed decrease in the intensity of ester peak ($1{,}720\,cm^{-1}$) and then the presence of P–C bonds by characteristic absorption at $1{,}465\,cm^{-1}$.

Different types of linkages have diverse effects on the thermal stability of polymers derived from imido-PN. Bisimido-bisphthalonitriles are usually synthesised by condensation reaction between bisphthalic anhydride and aminophthalonitrile. First, it forms a bisamic intermediate which consequently changes to imide groups. Structures of aminophthalonitrile and dianhydrides have a great impact on product formation. For instance, it was found that 4-AmPN does not form bisamic acid as expected; instead, it favours formation of a charge transfer complex. If the amino group is free from the effect of nitrile groups, just like if positions of amine and nitrile groups are well separated as in 4-3′APPN, then there is no difficulty for bisamic acid formation. The driving force for formation of bisimido-bisphthalonitriles is mainly the electron-donating and electron-accepting nature of respective amine and anhydride involved in these reactions. The higher the ionisation potential of the amine, the lower the acylation rate is. Electron affinities of aromatic dianhydrides depend on the nature of their linking units; their order relative to pyromellitic dianhydride (PMDA) being – CO– > C(CF$_3$)$_2$–O– > (CH$_3$)$_2$Si as linking groups. The order of thermal stability varies in the sequence of ether > keto > dimethylsilane as connecting unit (R) is a monomer (Scheme 3.7(a)) [22–24]. Methyl groups in (CH$_3$)$_2$Si moiety serve as weak scission

(a)

(b)

Scheme 3.7: Structures of (a) imido-PN monomer and (b) PN-terminated PEI oligomer with phthalazinone moiety.

points and are responsible for lower thermal stability of the polymer chain. The solvent resistance and thermal properties of imide-PN resins could be further increased by higher extent of cross-linking through long-term heat treatment at 300 °C.

BMI-bearing bisphthalonitrile monomer was synthesised [25] using 4,4′-bismaleimidodiphenylmethane and 4-aminophenoxyphthalonitrile in the presence of a base (Scheme 3.8). This can form phthalocyanine resin by thermal polymerisation in presence of trace amount of methylene dianiline. Good adhesion was shown by the resin with copper strips and can be used as heat-resistant adhesives. Thermogravimetry data revealed excellent thermal and thermo-oxidative stabilities of the resin with char yield of 82% (778 °C) in nitrogen.

Scheme 3.8: A bisphthalonitrile monomer-containing BMI groups.

Attempts have been made to improve processability and properties of the PI through introduction of PN groups as pendant substituents (Scheme 3.9). In PI with pendant PN groups (CN–PI), their solvent resistance and thermal properties of the cured resin could be improved due to cross-linking of nitrile groups at elevated

Scheme 3.9: Preparation of CN–PI polymers. Reproduced with permission from K. Zeng, L. Li, S. Xiang, Y. Zhou and G. Yang, *Polymer Bulletin*, 2012, 68, 1879. ©2012, Springer [26].

temperatures. However, T_g was not observed for these cured networks up to 350 °C [26]. Another variant of PN-terminated PI oligomers was prepared from an excess of PMDA reacted with aromatic diamines by Selvakumar and co-workers [16]. The oligomers were converted into polymers by using 4,4′-diaminodiphenyl sulfone as a curing agent. Differential scanning calorimetry (DSC) evaluation of the oligomers and oligomeric prepolymers revealed that the cure window of the system was increased (28–100 °C) by the formation of the B-staged prepolymers. The $T_{10\%}$ from thermogravimetric analysis (TGA) for these resins are in the range of 498–511 °C in N_2 and 448–461 °C in air atmosphere with improved char yield of 41.7–50% in air and 70.6–83% in N_2 at 800 °C. Nitrile-functionalised PI–polydimethylsiloxane copolymers exhibited excellent thermal stability at >400 °C [27]. Blends of alicyclic imide moiety and PN showed highly efficient thermal synergistic polymerisation effect [28].

In a recent study, a PN end-capped imide (FIPN) monomer was synthesised using two different aromatic amines such as diaminodiphenyl ether and 4,4′-diaminodiphenylsulfone as curing agents. Curing of FIPN was faster in the presence of diamines, and the curing occurred at lower temperature. All of the cured samples were stable up to 400 °C and showed high char yield [29].

3.4 Benzoxazine-containing PNs

Polybenzoxazines (PBZ) are considered as an ideal matrix for advanced composites due to their ease of processability and low water absorptivity. More importantly, benzoxazines follow a ring-opening mechanism with no evolution of volatiles that enable casting of blister-free components [30–32]. However, the Mannich linkage ($-CH_2-$) in these polymer backbones is a fragile segment detrimental to their thermal stability. Therefore, many research studies are focused on modifying the Mannich bridges by introducing addition-curable groups such as acetylenic and allylic functions [33–35]. These groups can be polymerised in situ with benzoxazine under heat without any curing additives. In this line, some elaborate studies were carried out to explore the

possibility of introducing rigid PN groups in order to improve the overall thermal stability of PBZ. In addition, benzoxazine ring opening could produce phenolic hydroxyl groups, which could serve as the curing agent, and then promote the PN polymerisation at moderate curing conditions.

Phthalonitrile-functional polybenzoxazines (BzPN) depicted in Scheme 3.10 do not require high curing temperature as generally required for the PN-functional prepolymers, and the maximum post-cure temperature for achieving the desired properties was 250 °C [36–38]. This is due to the fact that for PN-functional benzoxazines, oxazine ring-opening and PN addition reactions are closely connected to each other. They exhibit two cure exotherms corresponding to oxazine ring-opening and PN addition reactions, irrespective of whether it is comprised of monobenzoxazine or bifunctional benzoxazine units [39]. PN functions have also been introduced as pendant groups to the benzoxazine monomers as shown in Scheme 3.10 [benzoxazine PN (a-BzPN), xylenol benzoxazine PN (b-BzPN), bisphenol benzoxazine PN (c-BzBPN), benzophenone benzoxazine PN (d-BzBPN), biphenyl benzoxazine PN (e-BzBPN) and triphenyl
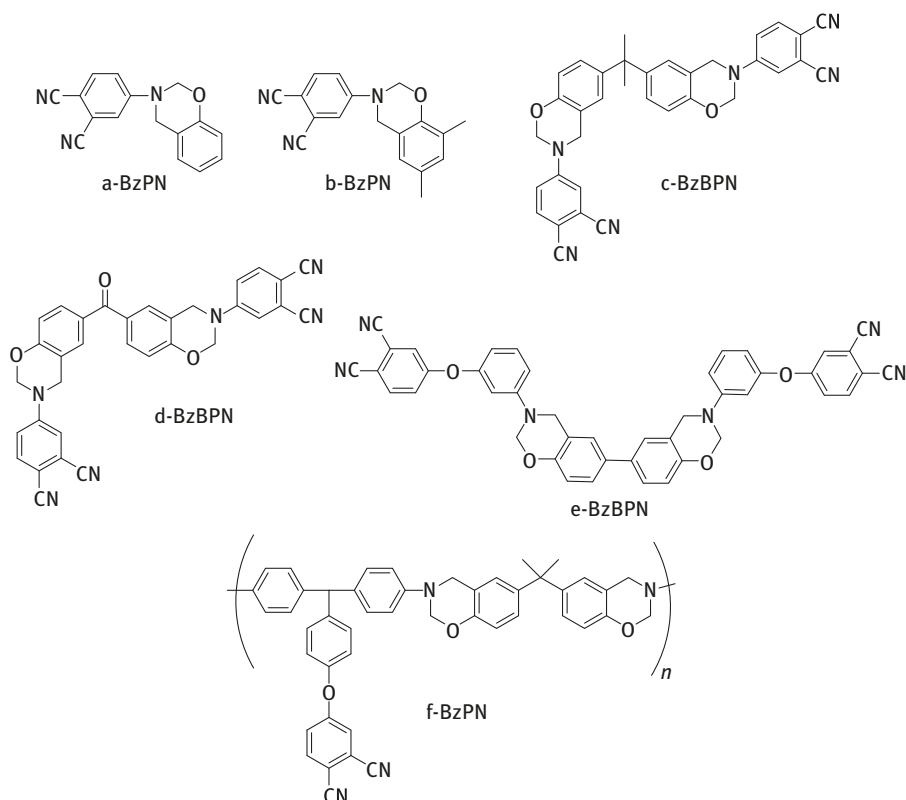

Scheme 3.10: Structure of benzoxazine–phthalonitrile precursors.
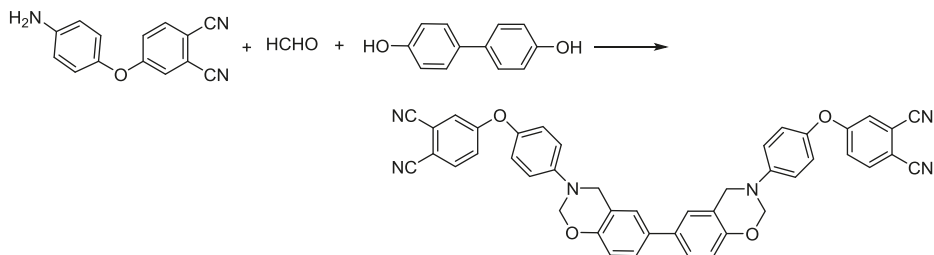
Scheme 3.11: Synthesis of biphenyl benzoxazine PN (e-BzBPN).

bisphenol benzoxazine PN oligomer (f-BzBPN)]. Scheme 3.11 shows the synthesis route for a bifunctional benzoxazine PN.

Phenolic hydroxyl groups generated by benzoxazine ring opening can effectively serve as the curing agent for PN reactions (Scheme 3.12) [36, 40]. Spectroscopic evidences throw light into cross-linking pattern of PN in the presence of benzoxazine units. On curing and post-curing, FTIR absorption bands centred around 950 cm^{-1} (CH out-of-plane deformation) and 1,507 cm^{-1} (in-plane C–C stretching), characteristic of trisubstituted benzene ring diminished with polymerisation time and finally disappeared with concomitant increase in the intensity of hydroxyl absorption around 3,280–3,400 cm^{-1} and decrease in the intensity of nitrile peak (2,231 cm^{-1}). The absorbance bands at 1,772 and 1,706 cm^{-1} are due to the carbonyl groups formed by degradation of the Mannich bridge under higher temperature curing process. The band at 1,651 cm^{-1} is probably attributed to the –C=N in the polytriazine and polyimine structures, and the isoindoline structure is observed at 1,619 cm^{-1}. The peaks at 1,580 and 1,352 cm^{-1} were indicative of triazine networks. These changes in the infrared spectra are attributed to oxazine ring-opening and the intramolecular reactions of nitrile-oxazine functions. ^{1}H-nuclear

Oxazine ring opening

Phthalonitrile cross-linking
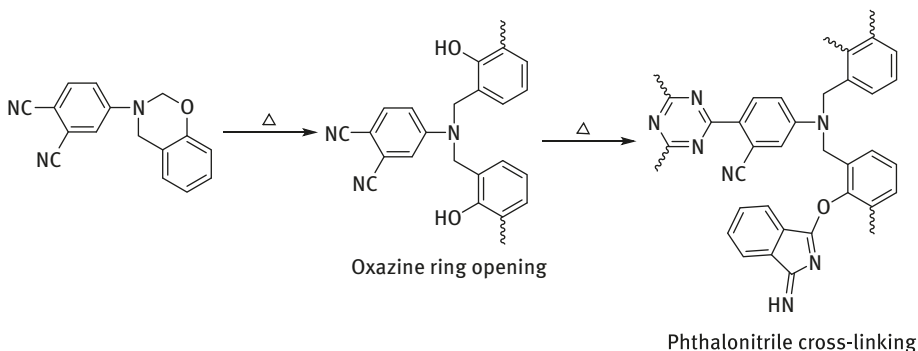
Scheme 3.12: Cross-linking reaction of PN-functional benzoxazine.

magnetic resonance peaks in the region of 4.4–4.5 denotes protons in an open oxazine ring structures, and the peak at 2.9 ppm is assigned to proton of OH formed by oxazine ring opening. Furthermore, the average values of activation energy for these reactions are calculated to be 102.2 and 90.6 kJ/mol for the first and second reactions, respectively, which are almost the same as that of benzoxazine (102–116 kJ/mol) and PN resins (87–105 kJ/mol), as reported earlier.

Cross-linked networks were with high thermal stability; 5% mass loss temperature ($T_{5\%}$) for monofunctional benzoxazine-based polymers is at around 450 °C and can be increased up to 550 °C for bifunctional precursors. Cured networks from xylenol benzoxazine PN (b-BzPN) were thermally less stable as they cannot form highly cross-linked structures due to restriction in oxazine ring opening imposed by *ortho*-substituent in precursor and free *meta* positions do not highly favour oxazine ring opening. Absence of fragile linkages like $C(CH_3)_2$ in d-BzBPN relative to other monomers helped build up a highly rigid cross-linked structure.

The nitrile groups that do not react during polymerisation undergo further reaction during thermal degradation and form high char yields. Additionally, these polymers offered low flammability. However, their curing temperature and melt viscosities were somewhat higher when compared with standard PBZ without nitrile substituents. To amend this, an attempt was done to copolymerise PN-functional benzoxazine with *ortho*-phenylnitrile-functional benzoxazine which can offer easy processability [37]. The high melt viscosity of PN-functional benzoxazines was decreased dramatically upon blending with phenylnitrile-functional monomer that boosted the T_g of the copolymer to as high as 294 °C (with 30 mol% of PN-functional monomer), which is a steep increase against 180 °C for neat *ortho*-phenylnitrile polymer [37–39, 41]. TGA–FTIR hyphenated analyses showed that complete conversion of nitrile groups occurred during reactions of unreacted PN functions with thermally degraded PBZ. A two-stage thermal decomposition pattern (400 and 600 °C) was exhibited by copolymers of phenyl nitrile and PN-functional benzoxazines. FTIR studies on the gas evolved during TGA showed that the major decomposition products are NH_3 (930 and 960 cm^{-1}), CO_2 (2,350 and 2,370 cm^{-1}) and substituted benzenes (very low intensity bands at 1,610, 1,500 and 1,050 cm^{-1}), as in the case of neat PN PBZ. The other characteristic peaks due to aminophenyl nitrile and carbodiimide (2,188 and 2,109 cm^{-1}) appeared depending on the isomer of phenyl nitrile used for copolymerisation.

Studies have shown that high-temperature-resistant magnetic polymer material can be prepared by the incorporation of magnetic materials during PN polymerisation (Scheme 3.13). One of the strategies adopted was to coat carboxylic acid-functional benzoxazine on neat iron carbonyl particles by the post-coating method and to promote interfacial reaction between magnetic iron and phthalocyanine prepolymer. By controlling the degree of PN prepolymerisation and composition of iron carbonyls, one could tune the magnetic properties of the cured polymer materials. The saturation magnetisation of the magnetic composites increased from 48 to 65 emu/g as the

(a)

(b)
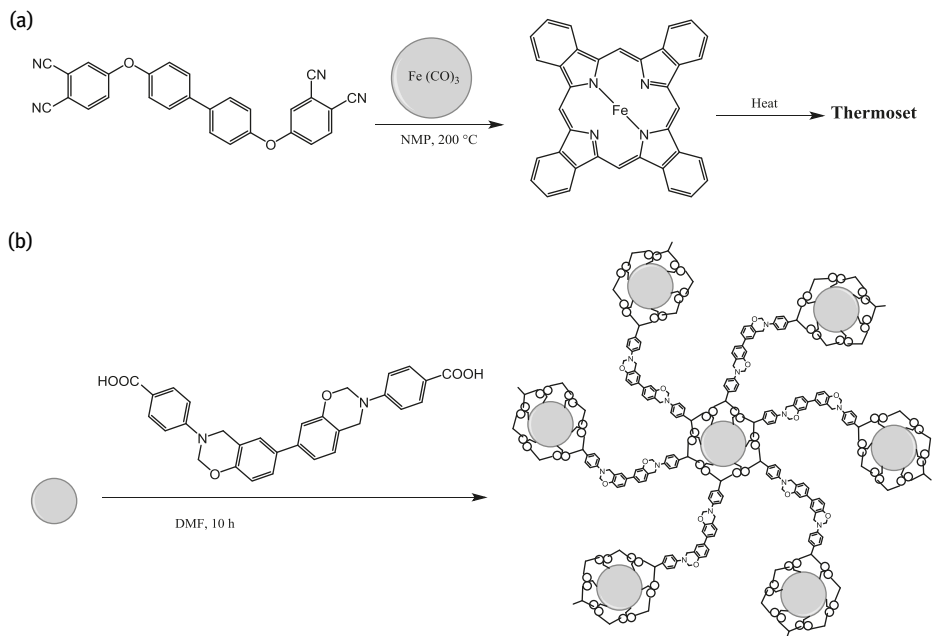
Scheme 3.13: (a) Formation of iron phthalocyanine magnetic material and (b) schematic of coating of iron carbonyl particles with benzoxazine benzoic acid. Reproduced with permission from K. Jia, R. Zhao, J. Zhong and X. Liu, *Journal of Materials Science: Materials in Electronics*, 2010, 21, 708. ©2010, Springer [42].

concentration of iron carbonyl increased from 20% to 40%. Meanwhile, the obtained magnetic composites also exhibited excellent thermal stability up to 500 °C [42–45].

High-performance PN resin containing benzoxazine has increasing applications in aerospace and electronic packing materials. To study the polymerisation mechanism of nitrile groups in the presence of benzoxazine, three model compounds with phenolic hydroxyl groups, amine structures and both of them were blended with bisphenol A PN monomers [46]. The synergistic promotion effects of the amine structures and the hydroxyl groups on the polymerisation of nitrile groups were confirmed in the study of its curing behaviour. During the polymerisation, the nitrile groups were first initiated by the lone pair electrons in amine structures and the further polymerisations were triggered by the phenolic hydroxyl groups. Also, the regular space configuration of amine structures and hydroxyl groups is favoured to the polymerisation process. A benzoxazine-co-self-promoted PN polymer was also obtained via catalysis polymerisation when mono-functional benzoxazine (P-a) was blended with self-promoted 4-aminophenoxy PN. The produced copolymers showed excellent enhancement in thermal properties and improved T_g [47]. In another report, benzophenone-centre bisphenol-A

containing PN monomer was successfully produced by a nucleophilic substitution reaction of 4,4′-difluorobenzophenone with 4-nitrophthalonitrile and bisphenol. The curing studies of the resultant gamma ray irradiate with 100 kGy dose of ^{60}Co gamma radiation. The copolymers possessed high glass transition temperature (164–227 °C) and high stiffness values (2.72–3.03 GPa) [48].

3.5 Low melting-type PN-containing siloxane moieties

One of the disadvantages faced by PN monomers is their high softening points (180–250 °C). This contributes to the narrow processing window of these systems and the polymerisation starts shortly after melting (around 230 °C), which causes an abrupt increase in viscosity. The development of oligomeric PN [49, 50] matrices resulted in a significant decrease in T_g to 41–80 °C but processing of such materials at RT without preheating was limited.

This necessitated the researchers to think of incorporation/anchoring of flexible units into PN backbone to facilitate their processing and lowering the melting point. One such attempt was made by Babkin [51, 52] by introducing a flexible siloxane (−O−SiR$_2$−O−) bridge, which presumably increases the chain mobility in the target molecule in comparison to existing PN. Si−O bonds have poor hydrolytic stability but it can be enhanced by having substituents around siloxane bonds as these can effectively shield Si−O bonds from hydrolysis. In addition, low T_g can be achieved due to the flexible siloxane linkages in the molecular structure, and transition point can be varied depending on the nature of substituents. The T_g of monomer was 27 °C when both substituents in Si−O bonds are phenyl rings while when a methyl group is introduced as one of the substituents, T_g further fell to 12 °C. Larger substituents on these linkages decrease the conformational freedom of molecules and lead to higher T_g (Table 3.1). Thermal and thermo-oxidative stabilities of their cured resins were comparable with other PN resins (Table 3.2). As phenyl groups are more labile and bulky, steric hindrance did not allow for a stable network formation during curing.

Methylene linkages too impart flexibility to the molecular chain. For the monomer devoid of −CH$_2$− bonds between aromatic ring and siloxane bridge showed growth in T_g from 11 to ~27 °C (1e and 1i). They were hydrolytically unstable in air and decomposed to initial phenol starting compound and therefore curing of resorcinol-based siloxane resins was impossible.

This reduction in T_g could be explained by the presence of the flexible siloxane bridge in the molecular structure. With the support of modelling studies, study on low melting PN was elaborated by evaluating the effects of other linkages like phosphate units. Larger substituents on these linkages decrease the conformational freedom of molecules and leads to higher T_g. Phosphate units are thermally stable fragments (1 h in Table 3.1) and their polymers possessed high T_{hd} (~450 °C) and
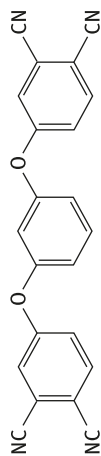
Table 3.1: Comparison of glass transition temperatures [51, 52].

Monomers/oligomers	Substituents	Reference	T_g (°C)
	R, R' =Ph	1a	27
	R = Ph, R' =CH$_3$	1b	12
	R, R' = CH	1c	2
	R, R' =Ph	1d	21
	R = Ph, R' =CH$_3$	1e	11
	R, R' = CH	1f	−1
		1g	21
		1h	42
		1i	27

1j		185
1k		42
1l		4
1m		40
1n		35

Table 3.2: Thermal and thermo-oxidative stability of cured resins.

Reference	T_g (°C)	T_{hd} (°C)	$T_{5\%}$ (°C) (inert)	Y_c % (inert) (900 °C)	$TOS_{5\%}$ (°C)	Y_c % (air) at 1,000 °C
1a	27	415	531	75	524	11
1b	12	428	537	79	520	12
1c	2	413	545	81	527	13
1d	21	455	524	80	523	29
1h	42	–	498	72	494	15
1i	27					
1j	185	441	523	75	504	0
1k	42	441	493	62 (1,000 °C)	486	–
1l	4	471	503	76	495	22
1m	40	428	541	82 (1,000 °C)	543	11

T_{hd}: heat distortion temperature.

thermal stability [$T_{5\%}$ = 524 °C, Y_c (argon) = 80%]. Disiloxane linkages (Si–O–Si) are also mobile like O–Si–O bonds and their incorporation decreased the T_g to 4 °C, which is lower than that for any reported PN monomers. The monomer containing Si–O–Si bridge demonstrated excellent rheological properties, namely, a wide processing window with low viscosities in the temperature range of 80–220 °C which makes it suitable for composite manufacturing by the resin transfer and vacuum injected moulding methods. Cured resin networks showed T_{hd} of 471 °C and possessed high thermal stability without any weight loss up to 470 °C and char yield of 76% at 900 °C under inert conditions. Degradation temperature was somewhat less compared to monomers with lower silicon content, probably due to steric hindrance by disiloxane fragment with substituents unfavoured the formation of durable-cured networks.

3.6 PNs with miscellaneous backbones

Diether-linked PN resins with spacers between the diether moieties varying from bisphenol A, bisphenol S, bisphenol A6F, resorcinol and hydroquinone have been reported to exhibit even better properties than the first-generation PN in terms of thermal and oxidative stabilities and moisture sensitivity [53, 54]. Thermal stabilities decreased in the order biphenyl > resorcinol > bisphenol S > bisphenol A > bisphenol A6F. Water absorption was higher for bisphenol S-linked polymers due to the presence of polar sulfone groups. Among the PN with different bisphenol backbones, the rate of polymerisation followed the order: bisphenol A6F > biphenyl > bisphenol A. Fluorine atoms helped increasing the electrophilicity of nitrile groups and make it more susceptibile to cross-linking reactions. If multiple phenoxy and sulfone
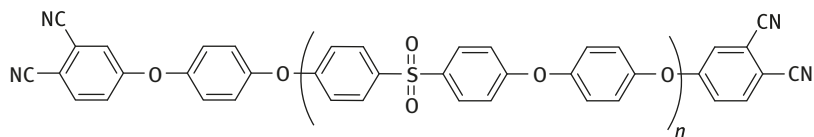
Scheme 3.14: PN monomers with multiple phenoxy and sulfone linkages.
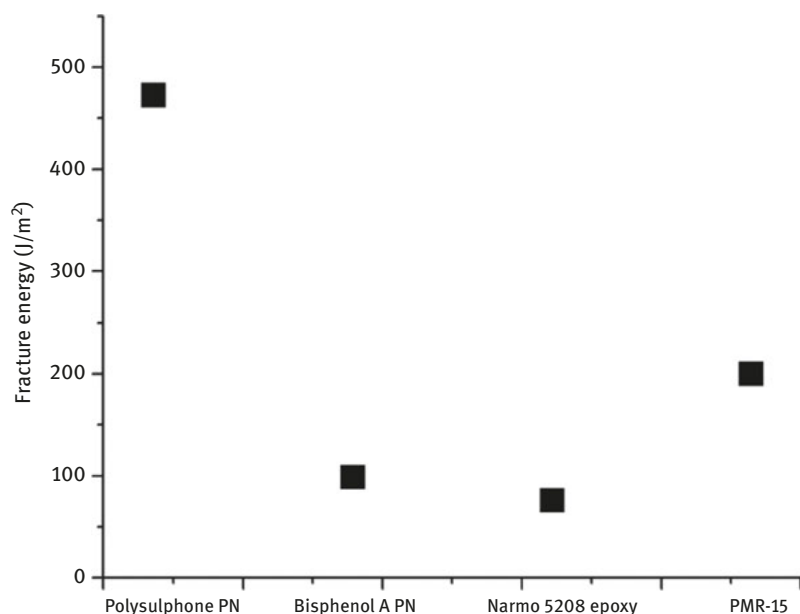

Figure 3.1: Fracture resistance of different polymers. PMR, polymerisation of monomeric reactants. Adapted from T.M. Keller, inventor; The United States of America as represented by the Secretary of the Navy, assignee; US4409382A, 1983 [55].

linkages are added to the PN polymer structure, it enhances the fracture toughness of the resultant cured network significantly (Scheme 3.14). This is quite evident from Figure 3.1, showing the fracture toughness of diverse high-performance polymers [55].

Malinge and co-workers have patented the synthesis procedure for the formation of polyaryloxy pyridine-*co*-polyphthalocyanines with relatively shorter gelation time and cure temperature below 250 °C [54]. Sumner and team attempted to realise vinyl ester-modified networks with improved flame resistance as an alternative to its brominated analogue which releases an undesirable amount of smoke [56]. For this, styrenic monomer with PN unit, that is, 4-vinylphenoxyphthalonitrile was realised by the nucleophilic aromatic substitution of 4-nitrophthalonitrile by 4-vinylphenolates. The

new monomer was blended into vinyl ester resins and copolymerised utilising ben-zoyl peroxide as a free radical initiator. During the copolymerisation (Scheme 3.15), initially the double bonds in methacrylate, styrene and 4-vinylphenoxyphthalonitrile undergo polymerisation followed by the partial involvement of nitrile functions at post-cure conditions (220–260 °C). Vinyl ester resin with 30 wt% of styrenic PN units showed a 70% decrease in peak heat release rate and lesser evolution of CO/CO_2.
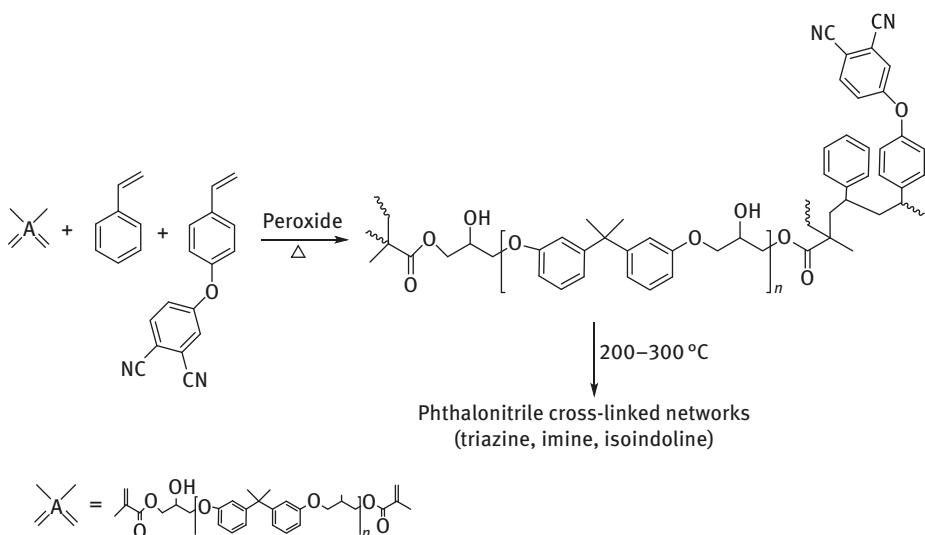
Scheme 3.15: Network formation of vinyl ester/styrene/4-vinylphenoxyphthalonitrile resin blends.

A good amount of research studies attempt to resolve the processing issues of PN sys-tems by incorporation of thermoplastic backbones. This was found to be effective in tackling the processing limitations and intrinsic brittleness of high-performance ther-mosets without sacrificing thermal and flammability properties. A well-known instance is the development of cost-effective polyether ether ketone (PEEK)-like PN resin by the US Naval Research Laboratory (Scheme 3.16) [57, 58]. The resin was claimed to be resistant to high temperature, non-flammable and having excellent damping and impact properties, which makes them suitable for numerous marine,
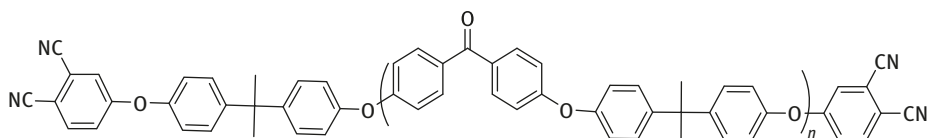

Scheme 3.16: PN end-capped PEEK.

aerospace and domestic applications. Dominguez and Keller have reported the synthesis of low-melting multiple aromatic ether-linked PN oligomers by the modified Ullman reactions. Here, different proportions of bisphenol were made to react with dihalobenzene to form hydroxy oligomeric intermediates, which was then treated with nitrophthalonitrile. Melting point of oligomer was thereby reduced to 40–42 °C, which provides a large processing window (>200 °C). The fully cured systems did not soften nor exhibited any T_g even up to 450 °C. However, from the exothermic heat flow, it was clear that with the increase in length of aromatic ether spacers, the cross-link density decreased, which made polymerisation more sluggish. The most exploited engineering thermoplastic for toughening purpose was PEEK [59].

Easily processable, low-melting PN resins with aromatic ether phosphine oxide units were realised by utilising a simple nucleophilic displacement reaction [60]. This was realised through reaction of an excess amount of either bisphenol A or resorcinol with bis(4-fluorophenyl)phenylphosphine oxide followed by reacting with 4-nitrophthalonitrile as represented in Scheme 3.17. The monomer exhibited softening at around 75–90 °C and was flowing freely at around 150 °C. Polymerisation to a thermoset did not occur until the composition with the curing agent [*para*-bis[(aminophenoxy)phenyl]sulfone (*p*-BAPS)] is heated above 230 °C. The thermoset polymer did not exhibit a T_g even when fully cured and maintains structural integrity at elevated temperatures. Oxidative ageing of polymers heated from 250 to 400 °C in 8 h temperature segments after being cured with 3% *p*-BAPS to a maximum temperature of 375 °C, and subsequent scanning electron microscopy images showed more extensive damage with cracked outer layers of aromatic-containing PN resins when compared to the phosphorus-containing PN.
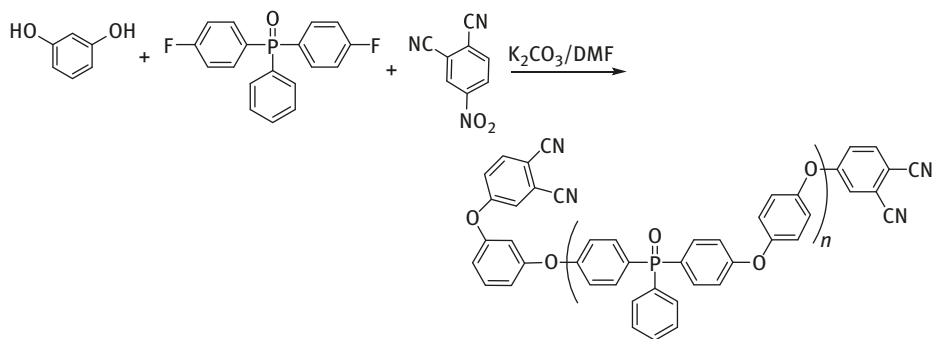
Scheme 3.17: Synthesis of PN oligomers with aromatic ether phosphine oxide units.

Aramide polymers with pendent PN groups (Scheme 3.18) were prepared by high-temperature bulk and low-temperature solution polycondensation methods [61]. The former method afforded a polymer with low molecular weight
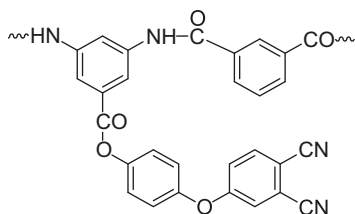
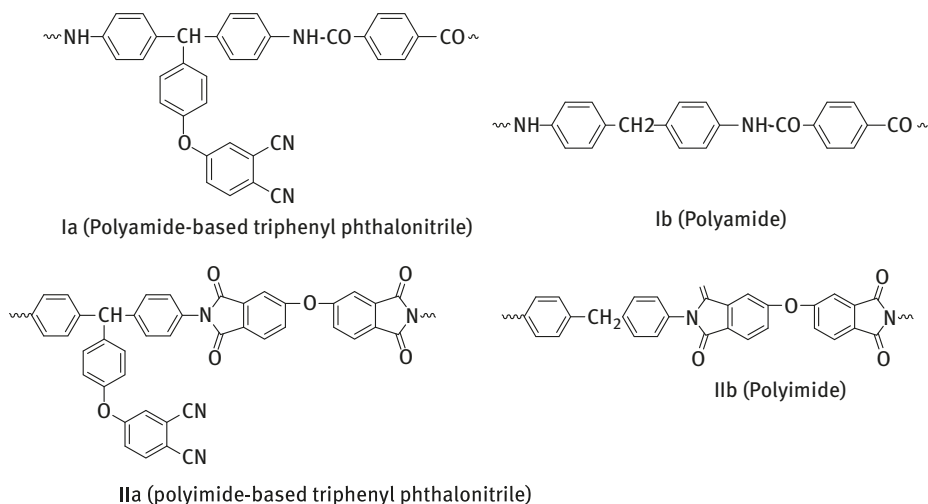**Scheme 3.18:** Typical structure of an aramide PN.

(inherent viscosity: 0.17 dL/g) while the latter resulted in a clear, viscous polymer solution having an inherent viscosity of 0.38 dL/g.

If alkyne moieties are present in PN systems, it can provide additional reactive cross-linking sites allowing for better control over the final mechanical properties of the cured resin. Alkyne-containing multiple aromatic ether-linked PN oligomers (Scheme 3.19) showed two-stage polymerisation in the presence of *p*-BAPS [62]. This is due to the amine-mediated PN cross-linking step followed by acetylenic cross-linking. The amorphous oligomeric monomer was softened at 75 °C and was completely free flowing above 125 °C, which upon heating with *p*-BAPS started polymerising. Higher extent of cross-linking was evident in alkyne-incorporated oligomeric PN resin from their larger storage modulus values (1,850–330 MPa) than their non-alkyne analogues (1,340–190 MPa) and the former did not exhibit a T_g up to 400 °C. The cured oligomer retained 95 wt% at around 495 °C and exhibited char yield around 70% upon heating to 1,000 °C in an inert atmosphere.
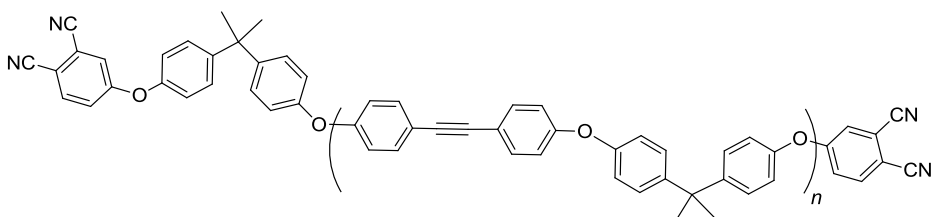
Scheme 3.19: Alkyne-incorporated aromatic ether-linked PN.

A comparative study on a series of polymers containing bulky phenoxyphthalonitrile units versus polymers without lateral substituents was done on the basis of conformational parameters, free and van der Waals volumes (Scheme 3.20) [63, 64]. Polymers with PN as side substituents exhibited improved solubility and processability as compared to related polymers without side substituents, allowing the former to be processed into thin films and coatings. The experimentally determined

Ia (Polyamide-based triphenyl phthalonitrile)

Ib (Polyamide)

IIa (polyimide-based triphenyl phthalonitrile)

IIb (Polyimide)

Scheme 3.20: Structures of polymers with pendent PN units: (a) polyamide (PA)-based triphenyl PN, (c) PI-based triphenyl PN, (b) PA and (d) PI backbones. Reproduced with permission from I.-D. Carja, C. Hamciuc, T. Vlad-Bubulac, M. Bruma and I.A. Ronova, *Structural Chemistry*, 2013, 24, 1693. ©2013, Springer [63].

T_g and decomposition temperature of these polymers correlated well with those calculated from the conformational rigidity parameters by Monte Carlo simulations. This method could be used to design similar polymers with tailored physicochemical characteristics. All the synthesised polymers were highly thermostable, their initial decomposition temperature being above 400 °C. The values found experimentally for T_g and decomposition temperature corresponding to the polymers with bulky lateral substituents correlated well with those calculated using the conformational rigidity parameters. The dependence of T_g and decomposition temperatures of these nitrile-containing polymers on Kuhn segment can be described by linear equations, with a very good factor of convergence.

Naphthyl-based PN monomer prepared from 1,6-bis(3,4-dicyanophenoxy)naphthalene cured with 4,4′-diaminodiphenyl ether (ODA) (Scheme 3.21) showed a broad, gentle curing exothermic peak (262 °C) and large processing window (106 °C) [65]. The post-cured networks were highly thermally stable with high T_g (>465 °C) and found to have very less water uptake behaviour (about 3 wt%). Organic amine (ODA) was used as the nitrile group curing agent for these monomers. The large processing window (105.7 °C) between the melting point (156.7 °C) and the broad, gentle curing exothermic peak (262.4 °C) is observed in the DSC for these new PN-based monomers and T_g was not observed up to 465 °C. The polymers were found to have very less water uptake behaviour as the water uptake was about 3 wt% after submersion in boiling water for 50 h.
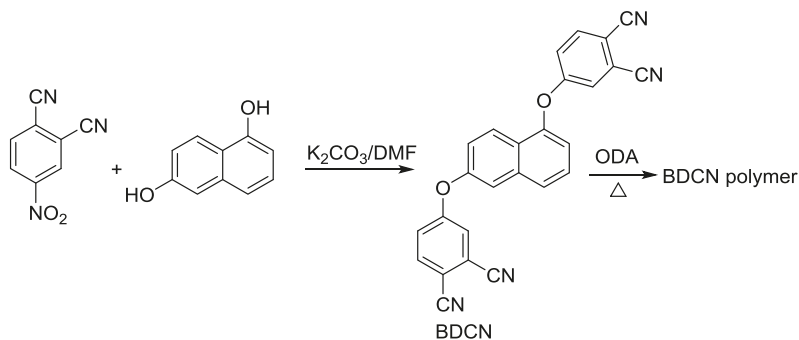
Scheme 3.21: Synthesis of bis(3,4-dicyanophenoxy)naphthalene (BDCN) polymer.

Keller and co-workers patented polyphthalocyanine resins derived from different structural variation of PN monomers and oligomers [66–68]. The chemical and physical properties of the polymers depend primarily on the bridging groups between the PN moieties. The groups providing the best properties are those with aromatic, polar and flexible moieties. The aromatic moieties provide the high mechanical strength, modulus and high thermal and oxidative stability and the polar moieties provide the excellent adhesive properties. Bisorthodinitrile with sulfone and keto groups can be used for high-temperature structural composites and adhesives. The known typical high-temperature adhesives like epoxies, PI and polybenzimidazoles are difficult to process. Epoxies are unsuitable as an adhesive material in temperature greater than 140 °C. PI and polybenzimidazoles are associated with difficulties in processing, and volatiles are evolved during their cure reactions. Adhesive composition consisting of a blend of bisphenol A-based PN which is a reactive component (amount ranges from 5 to 50 wt%) along with a non- bisphenol A PN monomer [69] was prepared and compared with a standard adhesive composition. These adhesive bonds have survived 300 °C for 16 h as the subsequent heat testing at ambient conditions resulted in cohesive failure of the adhesive, and exhibited T_g of 550 °C. The performance of the PN adhesive was compared to a standard epoxy adhesive. The latter when exposed to 240 °C for about 16 h and the shear adhesion tested gave near zero value. More oxidative-resistant polymeric PN with thermal stability above 300 °C can be derived by using dimide as linking units in bisphthalonitrile monomers. Polymers derived from bisorthodinitrile with stable oxygen-to-aromatic bonds in bridging chain are highly thermally stable, self-extinguishing and has a char formation greater than amide-bridged polyphthalocyanines [70].

The chemical structure of phthalazinone-based bisphthalonitrile is designed to impart several desirable properties to the obtained PN precursors such as good solubility and acceptable thermal stability [71–74]. This is because of unsymmetrical and kink non-coplanar conformation of phthalazinone greatly destroys the compact packing of the backbones and increases free volume. A more significant change in these

parameters can also be achieved by introducing functional groups into polymer chains that can be cross-linked thermally. As a typical cross-linkable group, cyano is often utilised owing to its easy introduction to the polymer chain as a pendent or terminal group and its trimerisation to high-temperature triazine resins. This cyclisation chemistry offers several advantages such as no need for metallic catalyst and absence of any volatile by-products. In this line, phthalazinone resins have been favourably modified by introduction of PN ends into the polymer chains. This can be done by a base catalysed nitro displacement of 4-nitrophthalonitrile (NPN) by N–H in phthalazinones (Scheme 3.22). These PNs were asymmetric and have a non-coplanar conformation to attain the minimum energy of conformation. As expected, they were readily soluble in common organic solvents such as DMAc, DMF, dimethylsulfoxide (DMSO) and NMP, and also in less efficient solvents including hot chloroform, acetone, methylene chloride and tetrahydrofuran. However, neat polymerisation of phthalazinone PN was extremely difficult and requires several days of continuous heating at 300 °C before a molecular weight increase was detected. The slow rate of polymerisation
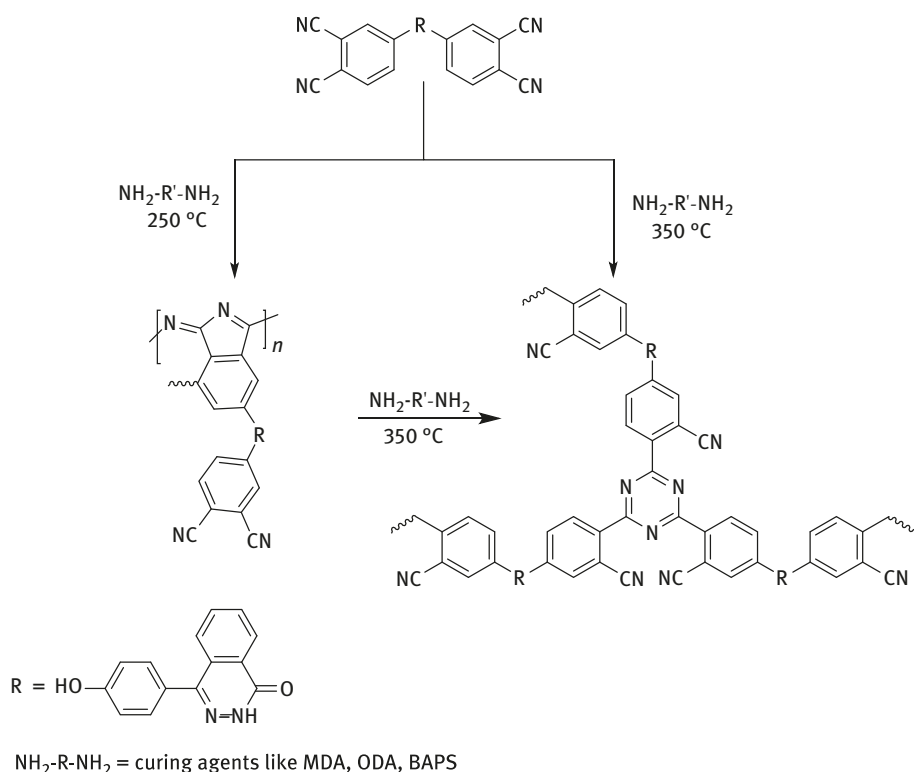
Scheme 3.22: Synthesis of PN-functional phthalazinone resin {BAPS: bis[(aminophenoxy)phenyl] sulfone}.

could be attributable to the heterocyclic structure's rigidity that reduces the mobility of the reaction sites. In the presence of amine curatives, it showed a well-defined cure exotherm at 293 °C arising from polyaddition reactions. Amines initially attack the nitrile components of bisphthalonitrile to afford an *N*-substituted-3-iminoisoindoline intermediate which further propagates to form highly cross-linked structures. The amorphous nature of the prepolymers can be mainly ascribed to the iminoisoindoline and phthalazinone moieties that disrupt chain planarity and symmetry.

A novel vinylpyridine-based phthalonitrile monomer, namely, 2,6-bis[4-(3,4-dicyanophenoxy) styryl] pyridine, was synthesized from 2,6-bis(4-hydroxystyryl) pyridine via a nucleophilic displacement of a cyano-substituent with NPN has been reported recently [75]. The obtained resin had a low melting point at 92 °C and outstanding processing window of about 146 °C, high storage modulus (2.9 GPa–1.8 GPa) high glass transition temperature (T_g > 400 °C), and excellent thermal and thermo-oxidative stability.

Bio-based PN monomers were also reported, namely, resveratrol based PN (RPN), dihydroresveratrol phthalonitrile (DRPN) eugenol-based PN (EPN) and guaiacol-based PN (GPN), through the nucleophilic substitution reaction of nitrophthalonitrile with resveratrol, eugenol and guaiacol derived from grapes, clove and lignin, respectively. The resultant polymers from EPN and GPN possessed low melting temperatures, wide processing windows (>186 °C), low melt viscosity (<0.03 Pa·s), higher glass transition temperature and better thermal stability. Ethyl group in DRPN imparts more flexibility to their structure and showed viscosity values similar to that of oligomeric second generation PN resins. [76, 77]. In another successful attempt, EPN monomer was successfully copolymerised with mono- and difunctional benzoxazine (P-a and BA-a) monomers via concerted catalysis polymerisation [78]. The addition of the bio-based EPN monomer enhanced the curing peak temperatures and reduced the curing reaction enthalpies. The thermal stabilities, stiffness and T_g of the copolymers were much higher when compared with the neat polymers.

3.7 Conductive PN resins

There have been a few reports on conducting behaviour of PN resins. Generally, conductive properties of PN varied as a function of temperature. Some of these methods reported are discussed here.

Keller and co-workers [79, 80] developed dithioether-linked PN monomer, which on polymerisation and subsequent pyrolysis changes to a conductive polymer. The monomer was synthesised by the reaction between NPN and a mercaptan and then copolymerised. The rate of polymerisation was increased by the addition of an amine catalyst. It was noticed that the electrical conductivity of the polymer increased to the conductor range by heating above 400 °C. In a similar report, a dithioether-linked PN monomer was prepared by the substitution reaction between

NPN and a dimercaptan [81]. The monomer to polymer conversion rate was increased by the addition of an amine as in the previous case. These polymers were made conductive as a function of the pyrolysing temperature.

A highly conductive polymer [82] based on PN was synthesised by the nucleophilic displacement of a nitro-substituent (NO_2) from NPN by the dipotassium salt of 4,4′-biphenol in dry DMSO. Electrical conductivity of the pyrolysed polymer was able to vary in a controlled manner as a function of both the time and temperature with conductive properties ranging from insulator to semiconductor and approaching metallic conductivity and is shown in Table 3.3. When the polymer was heated at 500 °C in an inert atmosphere, it started to show conductivity in the semiconducting range and as the temperature increased, the conductivity is found to enhance probably due to the formation of carbonaceous regions within the framework of the polymeric matrix. After heating at 700 °C, the polymer exhibited an RT conductivity of 1.5×10^{-1} S/cm. Moreover, the electrical conductivity did not change significantly when the polymer was exposed to air or water for prolonged periods of time. At still higher temperature of 900 °C, it displayed a conductivity of 265 S/cm, which is similar to that of doped polyacetylene. As a consequence of exposure to elevated temperatures, the polymer became brittle but retained properties suitable for a variety of structural applications.

Table 3.3: Effect of heat treatment for 24 h on room temperature conductivity of phthalonitrile resin (inert atmosphere) [81].

Temperature (°C)	Conductivity (S/cm)
400	$<10^{-8}$
500	$\sim 10^{-8}$
600	2.7×10^{-2}
700	1.5×10^{-1}
800	$6.7 \times 10^{+1}$
900	$6.7 \times 10^{+2}$

A diether-linked PN resin, prepared from BPh, was converted into an environmentally stable, highly conductive material by thermal pyrolysis. During the pyrolysis of a polymer, there is a progressive increase in conjugation and thus π orbital delocalisation, owing to the development of planar, polycondensed rings. As the pyrolytic temperature is raised, more and more unpaired electrons form π orbital delocalisation eventually reach a concentration level beyond which their recombination to form covalent network structures exceeds their rate of formation. As the polycondensed ring structures increase in size, the overall resonance energy of the system and the energy required for thermal excitation are reduced. As a result, the conductivity will be enhanced through mobile electrons, which can be converted to charge

carriers, in the overlapping orbitals of the growing polycondensed ring system. The overall conductivity will depend on the movement of the charge carriers within the individual polycondensed rings and from one ring system to another. This technology in realising a conducting PN polymer was patented by Keller and co-workers [83], where they claimed that diether-linked bisphthalonitrile monomers cured by amine-curing agent which is a non-doped conductive organic polymer have sufficient structural strength and thermal stability to replace conductive materials, particularly metals. Tensile strengths of these polymers after various cure and post-cure cycles were as follows: 94 ± 17 MPa (315 °C, 24 h, air), 94 ± 21 MPa (350 °C,12 h, inert), 80 ± 7 MPa (375 °C, 12 h, inert) and 72 ± 5 MPa (315 °C, 100 h, air) [84].

Compared to the state-of-the-art high-temperature performing PMR resins (48–83 MPa at RT), the tensile strength values were superior for PN resin systems. The fracture toughnesses of the PN materials were 0.61–0.63 MN/m$^{3/2}$ and a representative fracture toughness value for unmodified epoxy resins ranges from 0.5 to 0.8 MN/m$^{3/2}$. The resin system after subjecting to post-curing above 300 °C did not exhibit a T_g as determined by the absence of a viscoelastic transition from the glassy to the rubbery state [85].

In a similar report [86], the polymerisability and conductivity of a variety of mono- and multinitriles in the presence of free radical initiators at high temperature was determined. It was observed that mononitriles did not polymerise, but multinitriles do so readily. The black polymers had conductivities less than 10^{-9} Ω^{-1} and after heating those at 700 °C for several hours the conductivities are in the 10^{-6} Ω^{-1} range. Electrical properties of cyano group containing compounds [87], namely, tetracyanobenzene, PN, diaminomaleonitrile and acetonitrile after plasma polymerisation varied from 10^{-12} to 10^{-7} S/cm. Another conducting polymer was synthesised [88] by electrochemical polymerisation of 4-(2,5-di-2-thiophen-2-yl-pyrrol-1-yl)phthalonitrile (SNS-PN). Spectro-electrochemical studies showed that poly (SNS-PN) has an electronic bandgap of 2.45 eV and exhibited electrochromic behaviour. Soluble part of the polymer in DMSO has the fluorescent property emitting blue light, which enhances in the presence of several cations, in DMF, due to the better interactions between cyanide groups and cations. Completely conjugated bisphthalonitrile monomers as reported by Walton and co-workers [89] were linked together through a conjugated *para*- or *meta*-dianil structure as shown in Scheme 3.23.
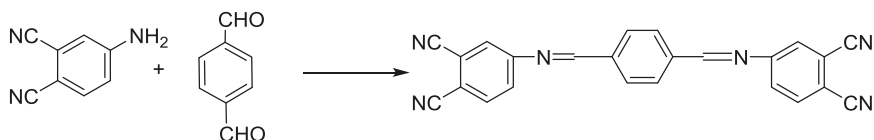
Scheme 3.23: Formation of completely conjugated bisphthalonitrile monomers.

This material had the potential to form a completely conjugated polymer network of high thermal stability from a prepolymer that passes through a liquid state and thus can be cast or moulded using conventional polymer processing techniques. The material was post-cured to induce conductivity and the conductivity on these materials can be varied from that of an insulator to approximately 10^2 $(\Omega \, cm)^{-1}$. The cured polymers had high thermal (only 9–10% weight loss after 100 h at 400, 500 and 600 °C) and environmental stabilities.

This chapter summarises different studies done on structural variations in PN monomers/oligomers and their resultant polymers. Structural modifications through incorporation of thermally stable groups such as fluorine, imide and benzoxazine enabled the development of resin systems with tunable properties. In short, fluorocarbon bridging chains imparted water repellency and oxidation resistance to the PN networks, and imide linkages in PN monomer structures made their polymer networks more thermally stable than the epoxies, BMI and other conventional thermosetting PI. Ester-imide linkages confer many desirable properties like solubility and solvent resistance to the resin. Benzoxazine rings via ring opening provided hydroxyl groups that facilitated PN cross-linking and exhibited excellent thermo-oxidative stability up to 500 °C and char yield of 77–80% at 800 °C. Ether, sulfone, phosphine oxide and amide moieties in the backbones have also been found to improve themomechanical characteristics of PN systems. Electrical conductivity of PN mainly depends on the pyrolysis temperature adopted and can be ranged from insulator to semiconductor and to the level of metallic conductivity.

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4 Self-catalysed phthalonitriles

4.1 Introduction

The cure temperatures of uncatalysed phthalonitrile (PN) resins are generally very high. Without catalysts, it is next to impossible to achieve their high conversions. A host of catalysts is known for PN resins. However, these are to be added externally and many of them are not miscible with the base resin. As PN resins have high melting points, a uniform distribution of the catalysts in the resin matrix to achieve uniform curing is practically difficult. Even if it is done, the catalysts may decompose and become inactive [1]. This can be overcome in case the catalysts are present as integral part of the PN chain. This approach ensures proximity of catalyst to the reactive site and thermodynamically favours catalysis as the entropy decrease in the activation step is less than that in a classical case. To circumvent this, the recent trends are more focused on designing resins with self-cure promoted behaviour. A good number of recent publications deal with such self-cure promoting strategies.

4.2 Phenolic hydroxyl-mediated self-curing PN

Phenolic compounds can be used as a nucleophilic initiator to catalyse the reaction between the nitrile groups of the PN monomer and phenol hydroxyl groups. The cure behaviours of hydroxyl-containing PN vary and are closely correlated to their molecular structure that, in turn, determines the thermal properties of the final cured products. Scheme 4.1 shows structures of some hydroxyl-containing PN monomers.

Highly acidic OH groups promote the polymerisation by the formation of protonated cyano groups undergoing nucleophilic attack by phenoxy or other cyano groups. The rate of disappearance of the nitrile peak in infrared (IR) absorbance at $2,230 \, \text{cm}^{-1}$ is one metric used to monitor progress of nitrile cure reactions. Bisphenol A (BPhA) as linking groups showed lower polymerisation rate than biphenyl, which is due to the presence of electron donating $-\text{C(CH}_3)_2$ moiety that makes nitrile less electrophilic in the former case [2]. In addition, through conjugation, the mutually electron-withdrawing nitrile groups on biphenyl moiety render these groups more electrophilic. Self-promoted curing phthalonitrile systems (ROHPN-RPN) can be developed in situ by reaction between resorcinol and 4-nitrophthalonitrile. This resolves the issues of blending of the monomer/curative mixture and the diminished reactivity of in situ hydroxyl catalysts, providing a larger processing window of 75 °C. Obviously, a larger processing window is favourable for processing PN monomers into void-free resins. Thermal stability of cured networks decreases with the increase in hydroxyl moieties, which are relatively weak bonds and could be destroyed in the heating process. Glass transition temperature (T_g) of
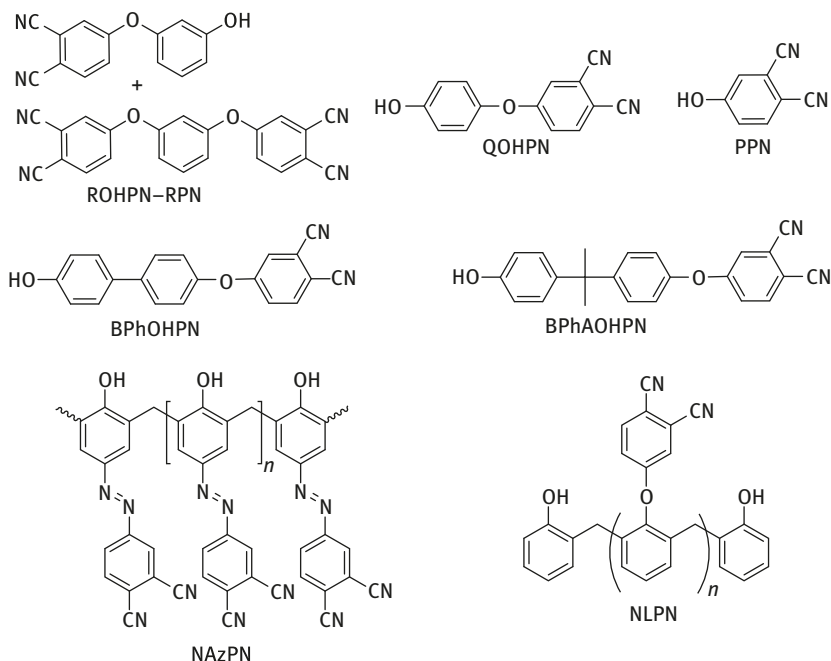
Scheme 4.1: Structure of hydroxyl PN monomers (BPhAOHPN:4-(4-(2-(4-hydroxyphenyl)propan-2-yl) phenoxy)phthalonitirle; BPhOHPN: 4-((4'hydroxy-[1,1'-biphenyl]-4-yl)oxy)phthalonitrile; NAzPN: phthalonitrile azo novolac; NPN: novolac phthalonitrile; PPN: 4-hydroxyphthalonitrile; QOHPN: 4-(4-hydroxyphenoxy)phthalonitrile; and ROHPN-RPN: mixture of 4,4'-(1,3-phenylene bis(oxy)diph-thalonitrile and 4-(3-hydroxyphenoxy)PN).

in situ catalysed resorcinol-based systems was 410 °C and was superior when com-pared to their binary curing compositions viz. 5 wt% 4,4'-diaminodiphenyl ether cured showed 320 °C and 10 wt% 4-(aminophenoxy)phthalonitrile-cured resin showed 347 °C [3]. It may be noted that for polymerisation of monomeric reactant(s) (PMR)-15, T_g is 340 °C, which restricts their usage in structural applications requir-ing stability at temperatures in excess of 340 °C.

Addition-curable phenolic resins are effective alternative to condensation phe-nolics for overcoming the processing problem of latter and to confer high char-yielding property [4, 5]. The general approach for designing such polymers is to anchor addition curable functional groups onto novolac and induce the thermal curing during processing. However, the thermally fragile cross-linking resulting in some cases of addition curable phenolic resins adversely affect the thermal stability of the resultant phenolic resins. This problem can be overcome through the choice of cross-linking functions that gives rise to thermally stable networks.

Much interest was shown to realise hydroxyl PN precursors on novolac resin as their highly aromatic character makes them a moderately thermally stable
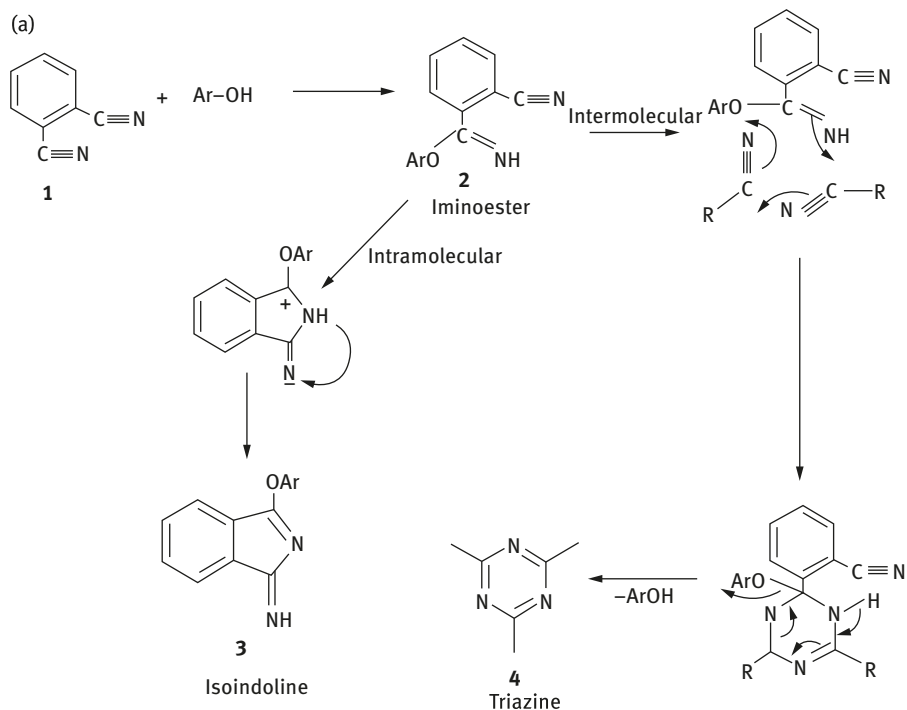
Scheme 4.2: (a) Probable phenol-mediated cure mechanism of PN oligomers and (b) probable cure mechanism of phenol-mediated cross-linking of PN oligomers. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *Polymer International*, 2013, 62, 7, 1068. ©2013, John Wiley & Sons [6].

backbone. NPN polymers bearing varying concentration of PN groups having self-curing nature was synthesised by condensation of novolac with 4-nitrophthalonitrile by Nair and co-workers [6]. PN-functional novolac resin is a single composition system, which can cure via addition mechanism without volatiles evolution. Free hydroxyl groups in novolac act as curatives for PN network formation. Multiple reaction mechanisms may be operational in OH and CN co-cure reaction as depicted in Scheme 4.2. Phenolic groups trigger the cyclisation reaction through the formation of iminoesters, which can undergo further reaction inter-molecularly with other nitrile functionalities to give triazine networks. Participation of the iminoester in an intramolecular reaction with a nitrile group leads to the formation of isoindolines. The isoindoline may further react with PN to form phthalocyanines. On curing, the intensity of the nitrile peak diminishes, but a complete disappearance of nitrile groups could not be attained. This can be attributed to the steric factors prevailing in systems containing higher PN content as the curing tends towards completion. Peaks at $1,600 \, \text{cm}^{-1}$ (C=N) and $3,300 \, \text{cm}^{-1}$ in Fourier-transform infrared (FTIR) are indicative of isoindoline and diimine structures and peak at $1,720 \, \text{cm}^{-1}$ is

(b)
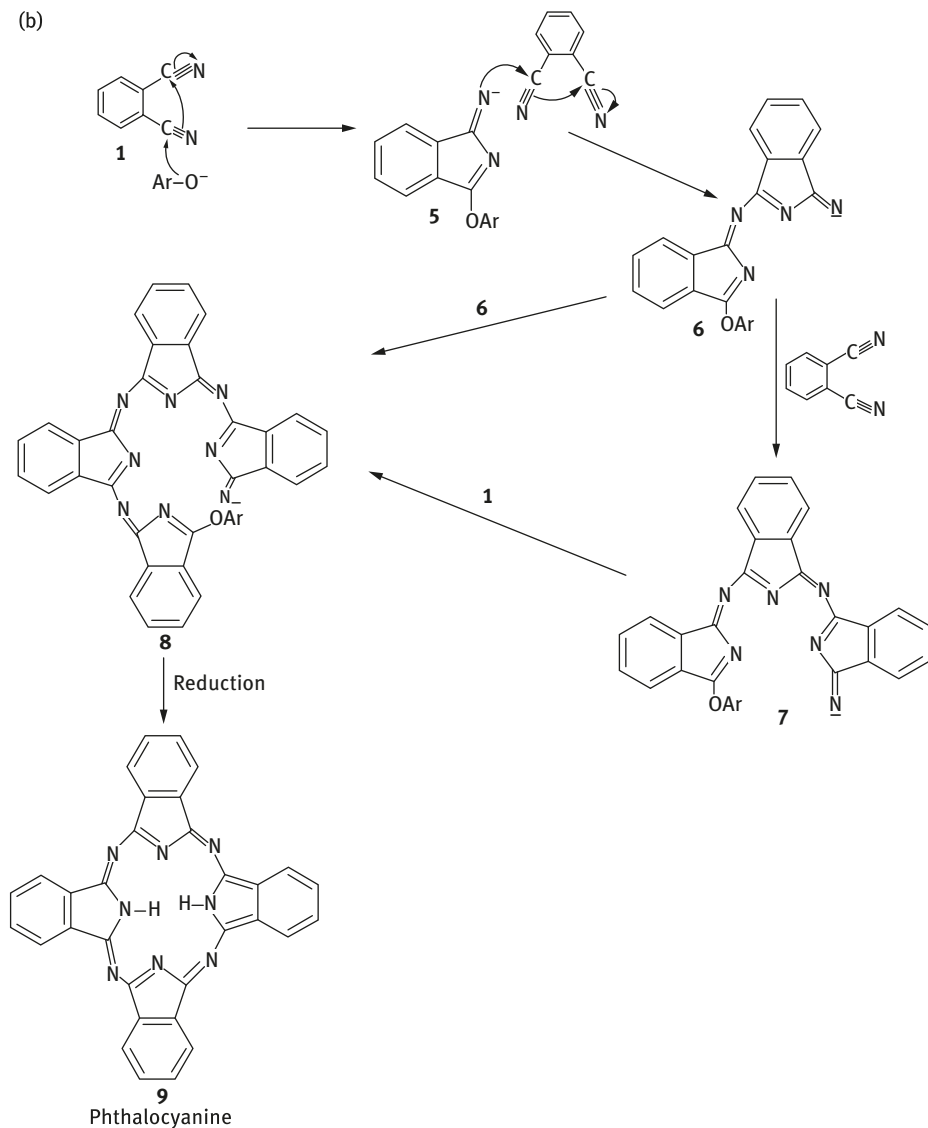
Scheme 4.2 (continued).

characteristic of isoindolines. Characteristic peaks due to triazine moieties appear at 1,325, 1,560 and 1,010 cm^{-1} correspond to NH stretching and bending vibrations in the phthalocyanine ring.

Differential scanning calorimetry (DSC) of the oligomers indicated that as the phenolic fraction increased there is a proportionate lowering in the curing temperature. NPN composition with 56% OH groups exhibited an initial cure temperature

(T_i) of 143 °C compared to a T_i of 265 °C for NPN with 1% −OH. This confirmed the participation of −OH groups in curing of the −CN groups.

Thermal stability and char residue of cured novolac phthalonitrile (CNPN) polymers resins increased systematically with an increase in PN concentration (Figure 4.1). The formation of thermally stable triazine, phthalocyanine groups and so on are more favourable in −CN-rich systems, whereas in phenol-rich systems, isoindoline groups of relatively lower thermal stability are preferentially formed.
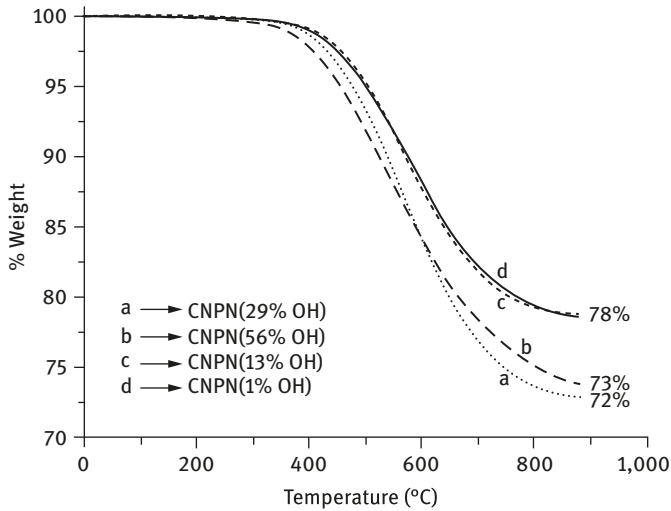
Figure 4.1: Thermogravimetric analysis traces of NPN polymers. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *Polymer International*, 2013, 62, 7, 1068. ©2013, John Wiley & Sons [6].

Carbon fabric-reinforced composites of phenol-rich compositions exhibited better mechanical properties as −OH groups promote fibre wetting and form more polar cross-linking groups like isoindolines, which are responsible for better consolidation of interphase (Figure 4.2). The T_g values of PN-rich systems were found to be above 300 °C. Flame retardancy of cured networks improved with an increase in PN fraction in the polymer as evident from the increase in limiting oxygen index value from 59% (NPN with 56% OH) to 72% (NPN with 1% OH). This is due to the formation of char at the expense of combustible volatiles, which in turn increases the oxygen levels required to sustain combustion.

Phenolic resin is widely used for thermoset structural components. However, they need further improvement for meeting the ever-increasing performance requirements. Usually novolac resin is cross-linked using additive like hexamethylene tetramine. As an alternative, phthalonitirle compounds are tried as cross-linkers and found to be very effective; nitrile groups can be readily catalysed by
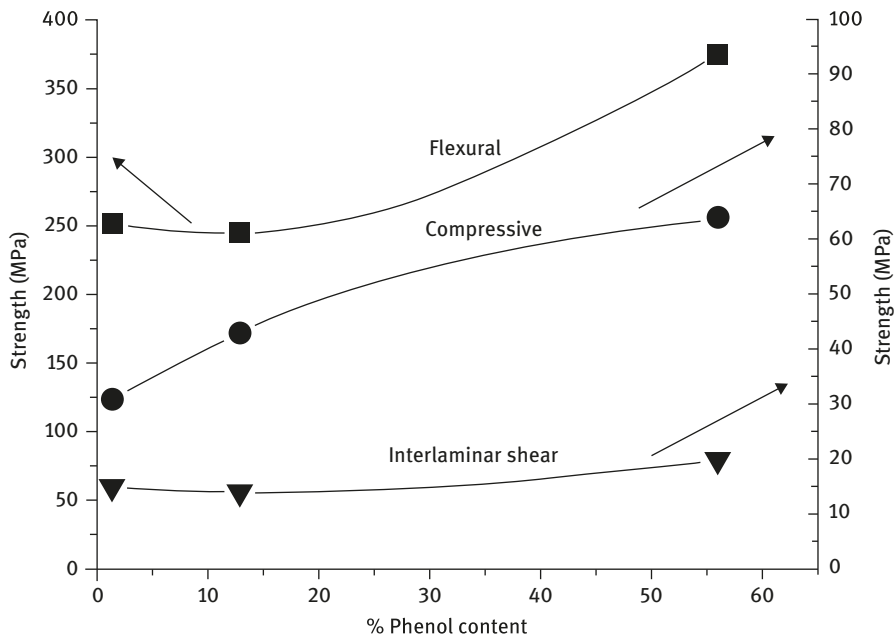
Figure 4.2: Dependence of mechanical properties of composites on polymer composition. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *Polymer International*, 2013, 62, 7, 1068. ©2013, John Wiley & Sons [6].

hydroxyl groups in novolac resin and form heterocyclic cross-linked structures. For a better picture of the reaction of phenolic novolac resins with biphenyl phthalonitrile (BPhPN), Sumner et al. demonstrated the reaction of 2-hydroxy diphenylmethane (6.1 equiv) with biphenoxy PN (1 equiv), which can form soluble-cured resins [7]. The protons resonating between 9 and 9.3 ppm are characteristic of N−H protons in isoindoline and the absorption bands in the FTIR spectra occurring at 1,600 and 3,300 cm^{-1} indicated imine structures. However, signals at up-field chemical shifts between 8 and 9 ppm were indicative of phthalocyanines. The sharp doublet at 9 ppm characteristic of triazine rings was not observed. It is important to mention that cross-linked network structures of novolac bisphthalonitrile differ with higher concentrations of bisphthalonitrile relative to nucleophilic phenols in the resin. Novolac oligomers cured with 15 wt% BPhPN or greater had T_g above 180°C and good fracture toughness ranging from 0.8 to >1 MPa m$^{1/2}$. Even a low level of 4,4′-*bis* (3,4-dicyanophenoxy)biphenyl significantly help cure the novolac oligomer. For instance, the cross-linked structure of novolac oligomer with BPhA diepoxide (65:35 wt/wt) exhibited T_g of ~120 °C and novolac cured with only 5 wt% BPhPN also showed T_g of ~120 °C [7]. The blends of bisphenol A phthalonitrile (BPhAPN) and novolac also exhibited self-promoted cure behaviour. Phenolic fractions in novolac accelerated the curing of the blends without any extra curatives and exhibited

moderately large processing window (98–118 °C) [8]. These post-cured copolymers [novolac/BPhAPN – 20:80 (wt/wt)] exhibited a 5% weight loss at 495 °C and char yield of 71% at 800 °C under anaerobic conditions. Novolac/BPhAPN copolymers cured up to maximum temperature of 290 and 330 °C displayed the flexural strength (49–91 MPa) and flexural modulus (4–5.78 GPa), which indicated that the mechanical properties of the copolymers were affected by the BPhAPN content.

PN novolac resin with 50 mol% phenolic groups possessed a broad processing window up to 85 °C (140–225 °C) with a low complex viscosity (0.44 Pas). The resin system was found to be exceptionally thermally stable with 5% mass loss temperature ($T_{5\%}$) at 448 °C and char yield of 71% [9]. When PN groups are anchored to novolac via azo linkages, the thermal profile of resin completely changed. NAzPN can be realised by the coupling reaction between novolac and PN diazonium salt (Scheme 4.3) [10]. The coupling of diazonium salt occurs preferably at *para*-position of the phenol due to the possible steric hindrance at the *ortho*-position and despite using excess diazomium salt in diazo-coupling reaction; the extent of substitution did not exceed 61%. Two exotherms observed during curing scan are attributed to the partial decomposition of azo bonds (224–249 °C) and addition polymerisation of nitrile groups with phenolic –OH groups in the temperature regime of 310–330 °C. The char residue of cured polymers with 23–56 mol% azo linkages exhibited 80% char at 700 °C. Conversely, when the degree of the substitution reached 61 mol% azo coupling, the char residue dropped to 58%; the reason could be preferential thermal cleavage of the azo groups.
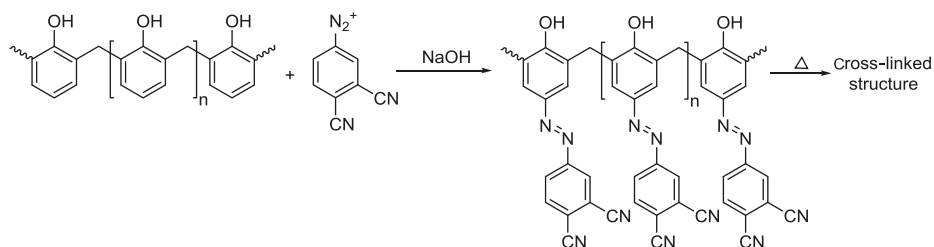
Scheme 4.3: Synthesis of NAzPN. Reproduced with permission from Y. Yang, Z. Min and L. Yi, *Polymer Bulletin*, 2007, 59, 2, 185. ©2007, Springer [10].

A novel multifunctional self-curing triphenol A based PN resin precursor synthesised from α, α, α′-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene (TPPA) with 4-nitrophthalonitrile (NPh) has been reported recently [11]. Self-cured TPPA-Ph resins exhibited relatively low melting points (less than 100 °C), high thermal stability, a wide processing window (116 °C) and excellent thermal and thermo-oxidative stability with high char yield.

4.3 Amine-functionalised self-curing PN

Amine being a stronger nucleophile than OH is expected to be a better self-cure promoting group for PN functions. General protocol for the synthesis of amine-containing PN monomers is nucleophilic displacement of nitro group of nitro PN by aminophenolates in basic medium (Scheme 4.4). This reaction could be speeded up at higher reaction temperatures; however, some side reactions, such as the oxidation of amino groups, are enhanced at higher temperatures. Thus, the reaction is carried out at room temperature (RT). Structures of amine PN monomers are shown in Scheme 4.5.
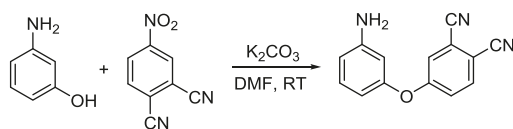
Scheme 4.4: Synthetic route for amine phenoxy PN oligomers (APPN) (DMF: dimethylformamide).
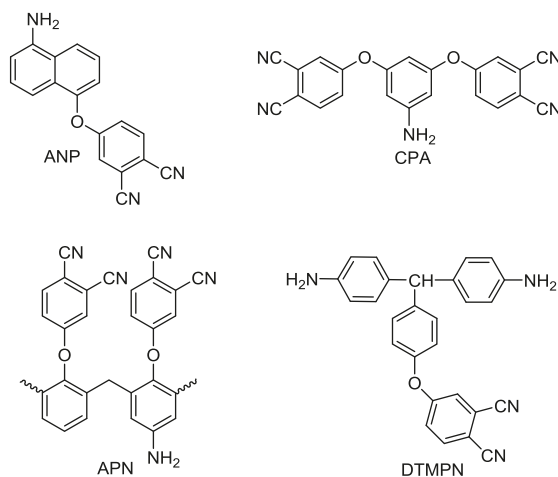
Scheme 4.5: Structures of amine PN monomers (ANP: amine-naphthyl phthalonitrile; APN: amine-novolac phthalonitrile; CPA: 3,5-*bis*(3,4-dicyanophenoxy)aniline and DTMPN: triphenyl-based amine-catalysed phthalonitrile).

Even the relative position of amine and PN in monomer structure influences the overall resin properties [12, 13]. *Meta*-positions facilitated better close packing and stronger hydrogen bonding resulting in a higher melting point (*meta*- 172 °C, *ortho*- 121 °C and *para*- 130 °C), imparting *ortho*- and *para*-compounds better processability. Amine

groups in *meta-* and *para-*position initiated nitrile reactions at a lower temperatures compared to that for *ortho-*derivatives. *O*-amine is likely to experience steric hindrance for smooth propagation of nitrile cure reactions. This is reflected from their onset cure temperatures (*meta-* 233 °C, *para-* 228 °C and *ortho-* 254 °C). Enthalpy of their cure reactions were higher than those of bisphthalonitrile monomers/diamine cure systems and self-promoted hydroxyl-containing PN. The presence of larger amount of amino groups in autocatalytic PN systems released more heat compared to binary composition systems. Enthalpy of curing was 251.6 J/g for *ortho-*, 203.5 J/g for *meta-* and 232.5 J/g for *para-*amine autocatalytic systems, and they follow first-order cure kinetics as elucidated by the Kissinger method [14]. T_g for their glass fabric-reinforced composites was above 560 °C.

Study done on APN system showed that incorporation of 24 mol% amine functionalities decreased the cure initiation to 180 °C against 310 °C for the uncatalysed novolac PN system, that is, a decrease of about 130 °C [15]. Cure mechanism of amine-mediated PN reaction invokes the attack of amine groups on nitrile functions in PN moieties to form amidine intermediates [16]. The imine linkages in the amidine undergo an intramolecular attack with the nitrile group, leading to the formation of isoindoline structures. The isoindolines can further react with other PN end-capping units to form tetrameric phthalocyanine networks [17]. The amidines can also proceed through an intermolecular reaction with other nitrile functionalities to form heterocyclic triazine rings [18]. Upon amine-mediated curing, PN systems form a polymeric network comprised of the afore-mentioned heteroaromatic moieties. Mechanisms of the formation of the heterocyclic intermediates are depicted in Scheme 4.6. In cured amine-novolac phthalonitrile (CAPN), an increase in the intensity of IR peak centred around 3,440 cm^{-1} was an indirect evidence for the formation of isoindoline and phthalocyanine moieties. The peak at 1,010 cm^{-1} was due to NH bending of phthalocyanine rings (Figure 4.3). These cross-linked networks impart rigidity and did not show any glass transition up to 350 °C. With the increase in amine content, thermal stability and char residue slightly enhanced due to participation of more cyano groups in amine-mediated cross-linking reaction and result in thermally stable heterocyclic structures. CAPN polymers retained 95% mass at 500 °C and it exhibited high char yield to the tune of 78% at 900 °C.

On heating, FTIR absorption peaks of −NH$_2$ in ANP monomer was transformed to absorption of −NH with clear diminution in nitrile peak intensity. The absorption peak from triazine units appeared at 1,357 cm^{-1}, but characteristic peaks for phthalocyanine or polyindoline formation was not observed (Scheme 4.7). In DSC scan, melting transition of monomer appeared at ~207 °C and triazine formation was indicated by exotherm at 251 °C [19].

The PN derivative derived from 5-amino resorcinol, that is, CPA acted as self-cure promoting monomer that melted at 214 °C and cross-linked between 257 and 274 °C temperature range [20]. The solidified product after DSC scan was almost
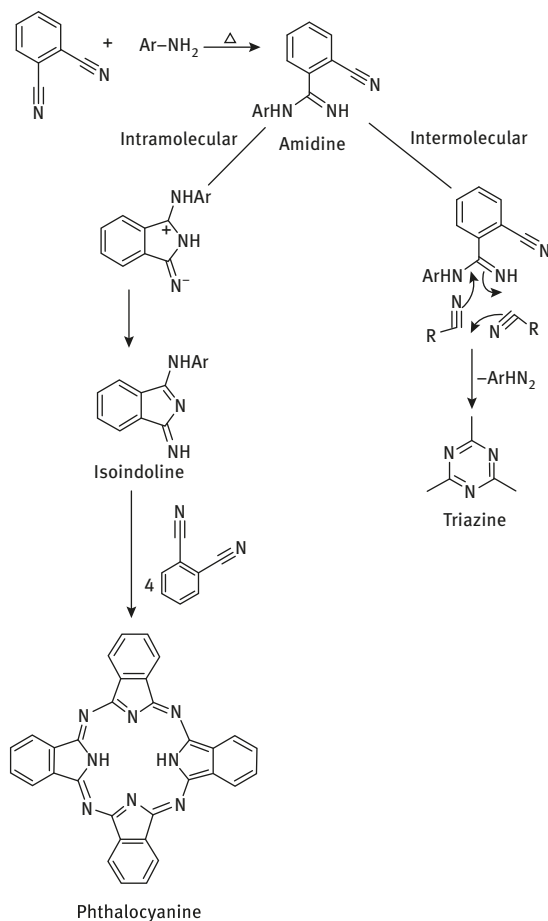
Scheme 4.6: Likely cure mechanism of amine-mediated PN reactions. Reproduced with permission from D. Augustine, K.P. Vijayalakshmi, R. Sadhana, D. Mathew and C.P.R. Nair, *Polymer*, 2014, 55, 23, 6006. ©2014, Elsevier [15].

insoluble in concentrated H_2SO_4, indicative of their extensive cross-linking. Self-promoted curing of the monomer 4-[4-(3,5-diaminobenzoyl)phenoxy]phthalonitrile (DAPN) occurred in a series of steps as shown in Scheme 4.8. With heating rate of 0.5 °C/min, melting transition and an exotherm with peak temperature at 226 °C were observed due to amine-initiated CN reactions and nitrile–nitrile reactions. However, only melting endotherm was observed with a heating rate of 3 or 10 °C/min. This is sometimes observed for faster reaction rates, wherein the cure exotherm is overlapped with melting endotherm [21].

DTMPN exhibited a lower melting point at 78 °C and could be cured at 250 °C. Cured networks were thermally stable up to 490 °C and gave residual weight of 76%
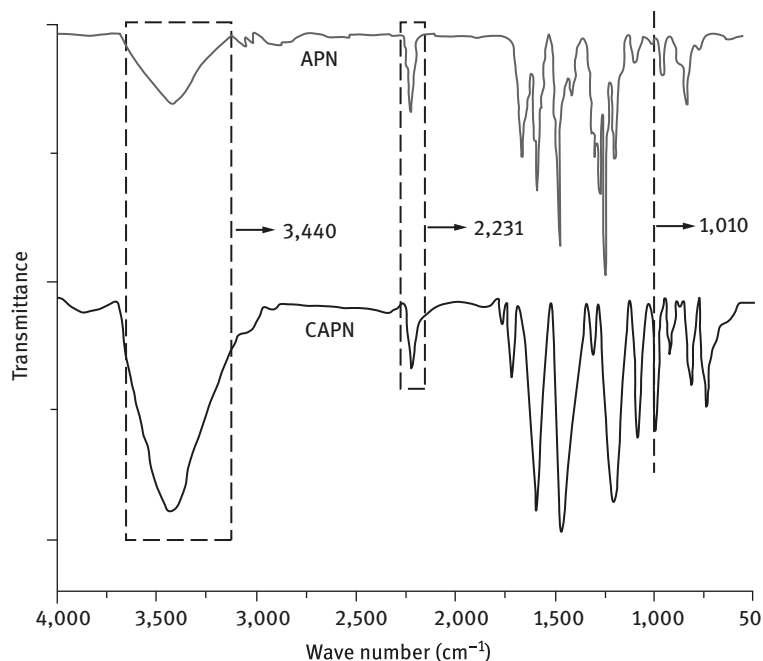
Figure 4.3: FTIR spectra of APN and CAPN. Reproduced with permission from D. Augustine, K.P. Vijaya-lakshmi, R. Sadhana, D. Mathew and C.P.R. Nair, *Polymer*, 2014, 55, 23, 6006. ©2014, Elsevier [15].
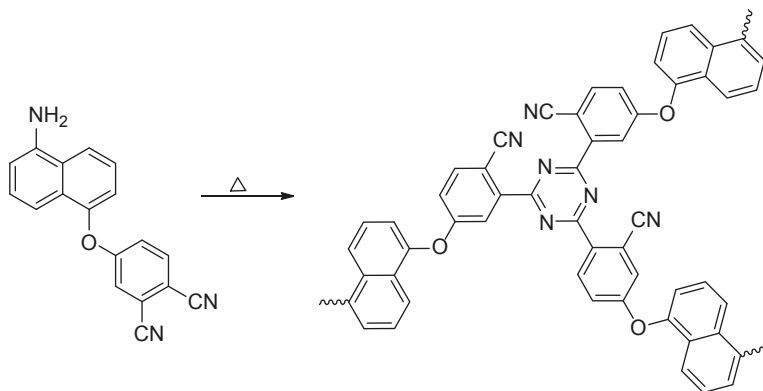
Scheme 4.7: Triazine network formation of ANP.

under inert conditions. Large processing interval is beneficial in terms of their composite fabrication processes. A useful method to reduce the melting temperature of polymer is lower their symmetrical structure and disrupt their close packing. This is mainly done by copolymerisation and introduction of flexible spacers, which
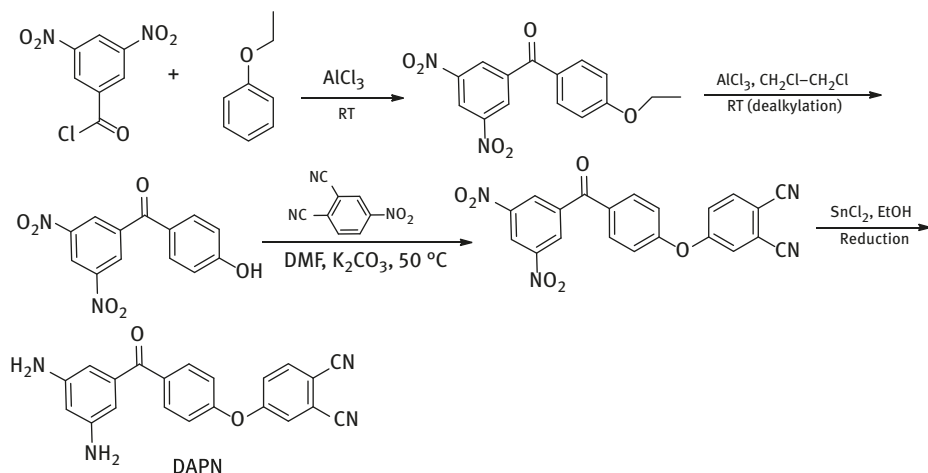
Scheme 4.8: Synthesis of DAPN. Reproduced with permission from S. Zhou, H. Hong, K. Zeng, P. Miao, H. Zhou, Y. Wang, T. Liu, C. Zhao, G. Xu and G. Yang, *Polymer Bulletin*, 2009, 62, 5, 581. ©2009, Springer [21].

improve their solubility too [22, 23]. Influence of structural variation was studied by deriving aromatic polyamides (PA) with pendant PN groups using reaction between DTMPN and terephthaloyl chloride. The number average molecular weight was in the range of 32,700–39,300 g/mol and polydispersity index was in the interval of 1.37–1.95. The inherent viscosity of polymers was in the range of 0.41–0.62 dL/g and exhibited film-forming properties. The presence of bulky pendant PN groups decreased the intermolecular forces between the polymer chains, causing a decrease in crystallinity and considerable increase in T_g by restricting the segmental mobility. This is substantiated by studies on DTMPN. T_g of PA based on DTMPN was 243 °C, while PA derived from BPhA was 222 °C [24].

Aurangzeb and co-workers developed amine-catalysing monomers with thermally stable groups such as amide and imide units [amine-containing amide phthalonitrile (EAPN) and amine-imide phthalonitrile (IAPN), respectively] directed to *ortho*-, *meta*- and *para*-position of PN groups (Scheme 4.9) [25, 26]. Intermolecular H-bonding imparts amide PN more crystallinity than their imide counterparts, which was indicated by their higher melting enthalpies. However, amide linkage in *ortho*-position restricts the intermolecular interactions to a greater extent compared to *meta*- and *para*-derivatives and therefore exhibited lower melting enthalpy. Among the three types of EAPN monomers, *meta*-derivative-initiated PN cross-linking at a lower temperature (253 °C) with higher cure enthalpy (221.5 J/g), whereas all the isomers of IAPN cured at same temperature (240 °C). EAPN monomers exhibited higher storage modulus than amino-phenoxy PN and imide analogues. All the
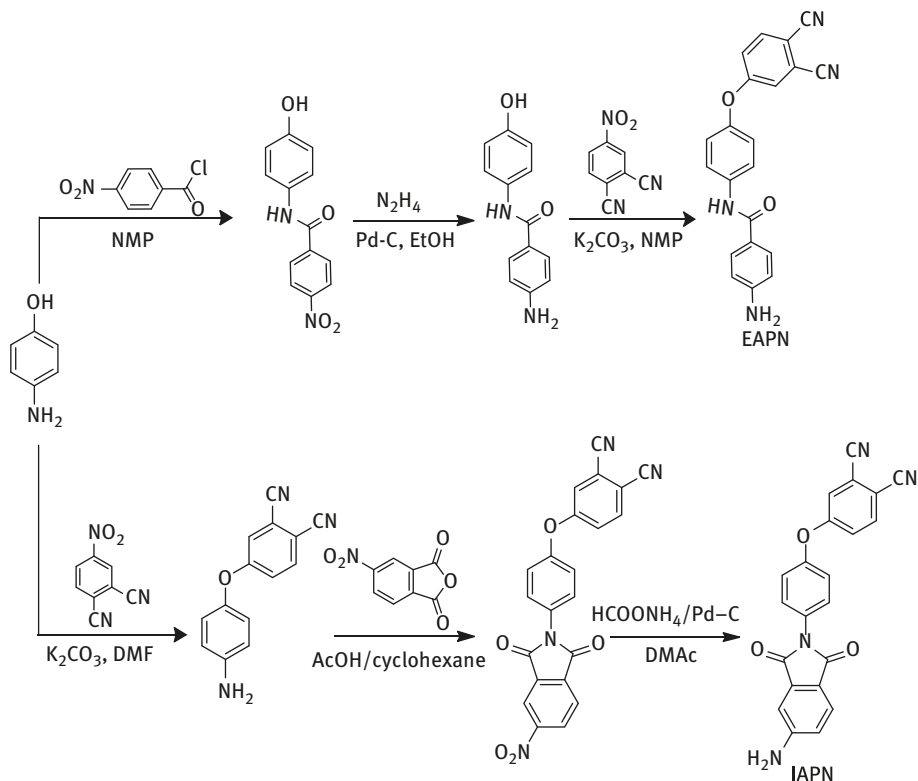
Scheme 4.9: Synthesis of EAPN and IAPN monomers (DMAc: dimethylacetamide; NMP: *N*-methyl-2-pyrrolidone; and Pd-C: palladium carbon). Adapted from B. Amir, H. Zhou, F. Liu and H. Aurangzeb, *Journal of Polymer Science, Part A: Polymer Chemistry*, 2010, 48, 24, 5916 [25] and A. Badshah, M.R. Kessler, Z. Heng, J.H. Zaidi, S. Hameeda and H. Aurangzeb, *Polymer Chemistry*, 2013, 4, 12, 3617 [26].

monomers maintained very low viscosity in the window between the melting point and the initiation of polymerisation. Processing interval spanned from 50 to 200 °C depending on their monomeric structure except *para*-IAPN, which showed a sudden increase in viscosity after melting. Their low melt viscosity and large processing window make them suitable candidates for resin transfer moulding or resin infusion moulding, among other liquid composite processing technologies. Imide linkages bestowed more thermal stability to the cross-linked networks ($T_{5\%}$ for IAPN was 525–529 °C and 409–502 °C for EAPN). However, char yield was higher for EAPN-cured systems (66–75% for EAPN and 62.5–70% for IAPN) due to their lower average molecular mass between cross-links. Thermal properties of different self-curable PN systems are listed in Table 4.1. T_g of composites of different resins are given in Table 4.2.

Table 4.1: Thermal behaviour of self-curable PN monomer/oligomers

Monomers	T_i (cure)	$T_{5\%}$ (°C)	Char
ROHPN-RPN	~250	493	74 (800 °C)
QOHPN[a]	–	325	55 (800 °C)
BPhOHPN[a]	–	341	58 (800 °C)
BPhAOHPN[a]	–	303	45 (800 °C)
PPN[a]	–	410	72 (800 °C)
NPN (29% OH)	~180	478	72 (900 °C)
NAzPN (46 mol% azo bonds)	206	240[b]	80 (700 °C)
ANP	251[b]	261[c]	73 (800 °C)
CPA	257	–	70 (800 °C)
o-APPN	254	527	74 (900 °C)
m-APPN	233	524	72 (900 °C)
p-APPN	228	528	74 (900 °C)
DAPN	226[b]	446	73 (800 °C)
DTMPN	–	480	76 (700 °C)
o-IAPN	240	528.8	70 (900 °C)
m-IAPN	240	525.4	66.6 (900 °C)
p-IAPN	240	527.7	62 (900 °C)
o-EAPN	318.6	517	75 (900 °C)
m-EAPN	252.9	506	66 (900 °C)
p-EAPN	308.6	531	69 (900 °C)
BIPN	–	~500	80 (800 °C)
Al-NPN	250[b], 284[b]	494	72 (1000 °C)
Al-BPN	270[b], 332[b]	477.8	75.9 (800 °C)
NPN-PR1	178	410	73 (900 °C)
NPN-OCN2	160	347	73 (900 °C)

[a]Heat treatment at 225 °C for 30 min, thermal polymerisation may be very slow and below the detectability limit.
[b]Initial decomposition temperature.
[c]Maximum decomposition temperature.
Al-BPN: allyl bisphthalonitrile; Al-NPN: allyl-phthalonitrile novolac; BIPN: benzimidazole bisphthalonitrile; NPN-OCN: cyanate ester-phthalonitrile novolac; NPN-PR: propargyl-phthalonitrile novolac.

4.4 Benzimidazole, allyl, propargyl and cyanate ester as self-catalysing groups

Although incorporation of amino or phenol groups to PN imparted autocatalytic nature, it was detrimental for their thermal resistance to a certain extent. There comes the significance of usage of benzimidazole ring with acidic hydrogen in PN resin, which has excellent thermal properties [27].

Table 4.2: T_g of resins/composites

Resin	Reinforcement	T_g (°C)
o-APPN	Glass cloth	582
m-APPN	Glass cloth	565
p-APPN	Glass cloth	580
o-EAPN	Neat	>500
m-EAPN	Neat	>500
p-EAPN	Neat	>500
o-IAPN	Neat	465[a], >500[b]
m-IAPN	Neat	435[a], >500[b]
p-IAPN	Neat	465[a], >500[b]

[a]Cured at 350 °C for 5 h.
[b]Post-cured at 375 °C for 5 h.
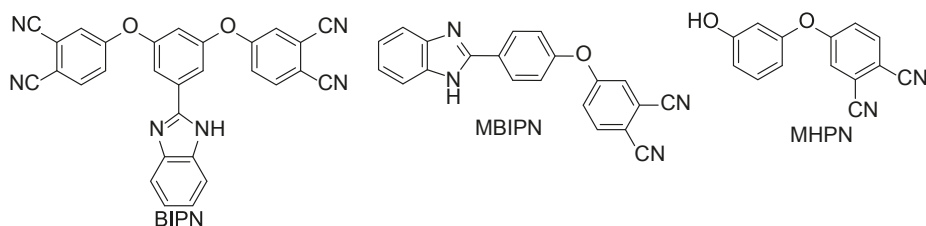
Scheme 4.10: Structure of BIPN, MBIPN and MHPN.

Benzimidazole bisphthalonitrile monomer (BIPN) was expected to be with similar or more intense self-promoting cure properties than hydroxyl PN (Scheme 4.10). On the contrary, it showed an extremely mild self-catalysing properties, but it was rewarding in terms of their processing techniques. Cure exotherm was not observed in their DSC curve, except for an indication of very slow polymerisation rate. This is totally in contrast to other catalyst in-built PN systems. Interestingly, in rheological measurements, a rapid increase in modulus was observed for BIPN after 5 h dwell at 300 °C, 2.5 h at 310 °C and 1 h at 330 °C, whereas 1,3-*bis*(3,4-dicyanophenoxy)benzene (lacks benzimidazole ring) did not show any increase in modulus even after 5.5 h dwell at a temperature of 310 °C. This clearly pointed out the role of benzimidazole in promoting PN cross-linking. For further clarification of BIPN polymerisation behaviour, a comparative study was done on simple compounds – model benzimidazole phthalonitrile compound (MBIPN) and model hydroxyl phthalonitrile compound (MHPN) representative of PN monomers with benzimidazole and – OH groups, respectively. No cure exotherm was observed for MBIPN, while *m*-HPN showed a well-defined exotherm with peak temperature at 240 °C. Even the presence of a strong acidic proton in benzimidazole was not favouring the cross-linking

of PN resin as that of other catalysed systems. This really contradicts the notion that self-catalysing is more pronounced in strongly acidic conditions. The study concluded that new interpretation was required to explain the unique polymerisation behaviour of BIPN.

Inspired from allyl phenolic bismaleimide system, studies were done to investigate the role of allyl groups on PN reactions. Al-NPN resin was synthesised from allyl phenolic precursors (Scheme 4.11) [28]. *O*-allyl groups modified the cure pattern of PN, which was evident from the cure profile of Al-NPN, allyl novolac (Al-N) and NPN oligmers. On heating, Al-N exhibited two exothermic peaks at 241 and 332 °C corresponding to Claisen rearrangement and allyl polymerisation and NPN exhibited only one exothermic peak at 273 °C due to phenol-mediated PN reactions [6, 29].
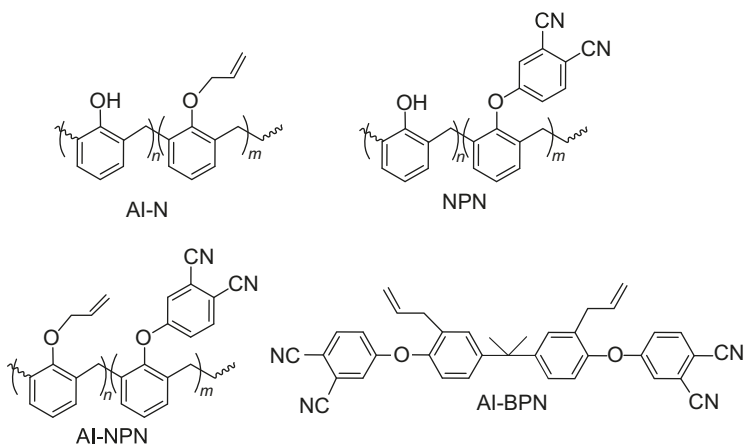
Scheme 4.11: Structures of Al-N, NPN, Al-BPN and Al-NPN.

Al-NPN clearly showed a multi-stage cure pattern: a small merged exotherm at 250 ° C, within the range of allyl rearrangement and a well-defined exothermic peak at 284 °C due to collective reactions from regenerated hydroxyl nitrile co-cured reactions, allyl nitrile (Ene reaction), nitrile–nitrile and allyl–allyl homopolymerisation [30]. On increasing the amount of allyl groups in Al-NPN from 35 to 60 mol%, nitrile conversion was enhanced from 60% to 76% and decreased the viscosity from 15 to 1 Pas. *O*-allylation decreased the intermolecular and intramolecular H-bonding interactions and the presence of aliphatic segments in Al-NPN increased their segment mobility and widened the processing window up to 89 °C. Based on Flynn–Wall–Ozawa method, activation energies (E_a) for first and second curing stages are 184.58 and 94.84 kJ/mol, respectively [31, 32]. First, E_a is higher due to the difficulty in allyl rearrangement in the presence of rigid PN groups and less number of free *ortho*-positions.

Second, E_a was close to phenol-catalysed PN reactions [33]. With the increase in allyl contents, aliphatic moieties in the cross-link structure increases and act as fragile points in the co-cured network. There is no possibility of Claisen rearrangement in monomers with C-allyl and PN groups as in Al-BPN [34]. Significant reduction in IR characteristic absorption peaks of =CH at $3,082 \, cm^{-1}$ and $-CH=CH_2$ at 1,638 and $1,410 \, cm^{-1}$ was observed along with evolution of new absorption bands at 1,010 and $1,360 \, cm^{-1}$, characteristic of triazine and phthalocyanine rings. This suggested that active hydrogen produced from the allylic polymerisation at relatively lower temperature catalysed the cross-linking of PN groups.

As addition curable groups are much compatible and could aid the polymerisation and amend overall properties of PN resins, a few studies were done to evaluate the impact of functions like propargyl (PR) and cyanate ester (OCN) in a PN polymer (Scheme 4.12) [35, 36]. In this direction, the influence of PR groups on PN cure process was studied through reactions of BPhA-based blends and model compounds; the details are included in Chapter 5 [33]. Based on this finding, self-curable one-component PR PN oligomers were realised by incorporating these groups simultaneously on a novolac backbone, propargyl phthalonitrile novolac (NPN-PR) [35]. Evidences were obtained for the possible reaction between C≡N and PR groups. On curing novolac backbone systems [cured propargyl phthalonitrile novolac (CNPN-PR)], IR peaks characteristic of ≡C–H ($3,272 \, cm^{-1}$) and C≡C stretching vibrations ($2,120 \, cm^{-1}$) disappeared completely with significant reduction in nitrile peak intensity (Figure 4.4). This clearly indicated the role of PR groups in drawing more nitrile groups into the co-cured network. Moreover, a broad peak in the hydroxyl region around $3,400 \, cm^{-1}$ was noted, which was also seen in the IR spectra of cured propargyl novolac (CNPR) oligomers (Figure 4.5). This observation supports the reported mechanism of PR polymerisation resulting in chromene networks via phenolic intermediates (Scheme 4.13) [29, 37, 38]. Since phenolic moieties can accelerate the nitrile curing, it was presumed that the hydroxyl intermediates formed in the PR homopolymerisation have acted
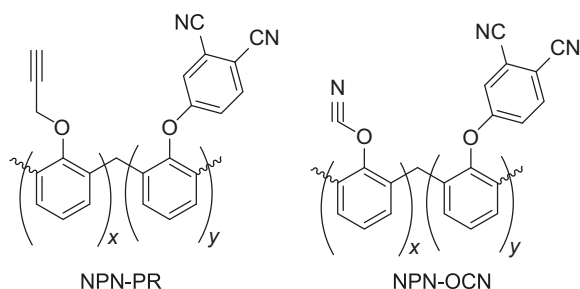
Scheme 4.12: Structure of NPN-PR and NPN-OCN oligomers [35, 36].
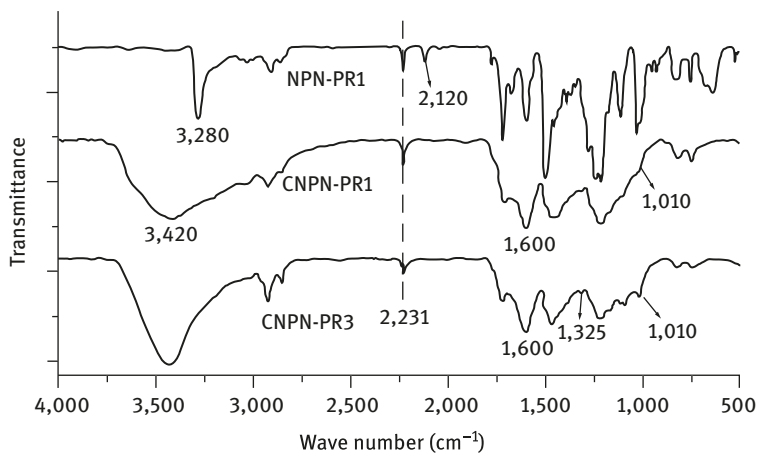
Figure 4.4: FTIR spectra of NPN-PR, CNPN-PR1 (PN:PR = 1:0.15) and CNPN-PR3 (PN:PR = 1:2.3). Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *European Polymer Journal*, 2015, 71, 389. ©2015, Elsevier [35].
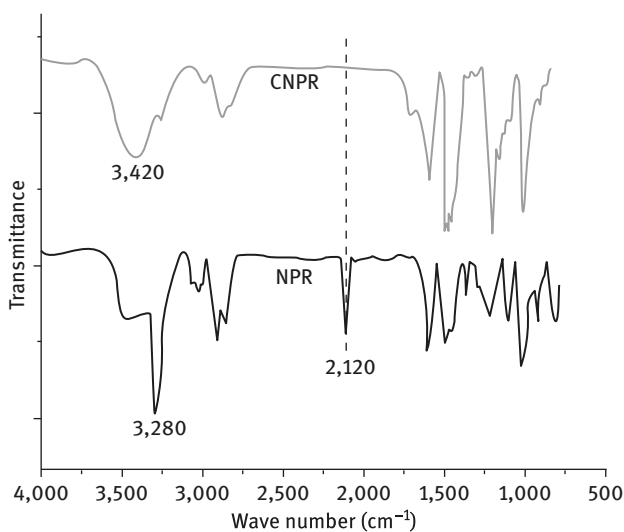

**Figure 4.5:** FTIR spectra of propargyl novolac (NPR) and CNPR. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *European Polymer Journal*, 2015, 71, 389. ©2015, Elsevier [35].

as the nitrile cure promoter. Reaction route for the formation of isoindoline, triazine and phthalocyanine networks from phenol-mediated nitrile reactions is depicted in Schemes 4.14. Their characteristic peaks at $1,325\,cm^{-1}$ (triazine),
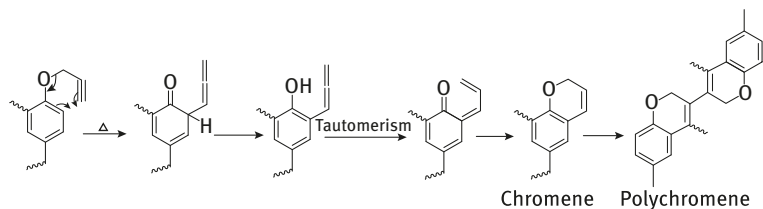
Scheme 4.13: Homopolymerisation of PR groups via phenolic intermediates. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *European Polymer Journal*, 2015, 71, 389. ©2015, Elsevier [35].
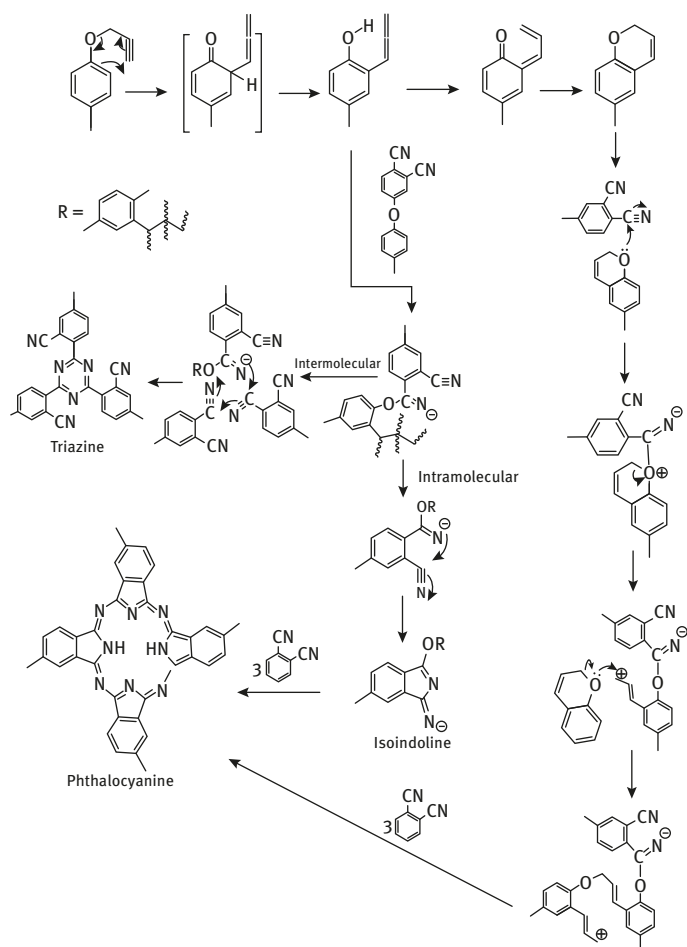
Scheme 4.14: Cure reaction pathways of PN in the presence of PR functions. Reproduced with permission from D. Augustine, D. Mathew and C.P.R Nair, *Polymer*, 2015, 60, Supplement C, 308. ©2015, Elsevier [33].

1,010 cm^{-1} (phthalocyanine) and 1,600 cm^{-1} (isoindoline) were observed in the IR spectra. Some IR peaks characteristic of triazine at 1,560 cm^{-1} and isoindoline at 3,300 cm^{-1} were unidentifiable in IR spectra due to the overlapping of peaks [7]. A decrease in curing temperature was observed with a proportionate increase in PR content. DSC showed an overlapping exotherm with two prominent maxima (at 260 and 310 °C). The first exotherm for the copolymer peaked at 260 °C was in the same temperature range as that for PR oligomers, due to the homopolymerisation of PR functionalities. The second exotherm was attributed to PN cross-linking promoted by hydroxyl intermediates and chromene units formed from polymerisation of PR groups. Furthermore, lower degree of swelling for NPN-PR polymers compared to cured NPN resin clearly showed that PR content in copolymer enhanced the number of cross-links and thereby decreased the amount of solvent penetrating into polymer network. Thermal stability of co-cured networks derived from PN-rich systems were relatively higher than those of pure PN oligomers. Higher content of PR groups in cured network has a detrimental effect on the thermal stability of the copolymers. PN-dominated systems exhibited initial decomposition temperature at 435 °C. This can be assigned to the formation of thermally stable triazine, phthalocyanine groups and so on in −CN-rich systems. Cured NPN-PR systems showed a mass retention of about 73–76%, marginally lower than char residue of the cured pure PN systems that gave 78% of char yield at 900 °C in N$_2$.

Although −OCN in cyanate ester and −CN in PN have similar mechanism of curing, −OCN groups did not co-cure with PN groups. This was observed in a study done on cyanate-PN novolac (NPN−OCN) [36]. Two well-resolved exotherms were observed at 120 and 335 °C, which correspond to cyclisation of cyanate groups and the second one to PN cross-linking. This is an indication that two functional groups undergo independent curing and do not influence the cross-linking of the other group. When free hydroxyl groups in NPN (with 0.69 mole fraction of OH) resin was transformed to OCN groups, the PN cure initiation shifted from 170 to 280 °C, that is, OH groups loses the advantage of co-curing with PN groups. This may be due to the high propensity of cyanate esters to undergo cyclotrimerisation to form phenolic triazine networks in contrast to the PN groups that demand higher E_a. Thus, though these two groups possess similar chemical nature and follow similar cure mechanisms (independently), they do not co-cure at all. NPN−OCN2 (OCN mole fraction = 0.43) oligomer doped with 0.3 and 0.8% of zinc octoate (NPN−OCN2− ZnO1 and NPN−OCN2−ZnO2) showed that the low-temperature exotherm due to − OCN groups showed a further shift to still lower-temperature regime with the increase in quantity of metal catalyst, while no change was observed in the case of PN cure exotherm (Figure 4.6). The presence of metal entities induced the cyclotrimerisation of OCN groups. This undoubtedly proved the independent curing of the two functional groups located on novolac backbone (Scheme 4.15). Introduction of −OCN groups did not confer any special characteristics to the resin except that their
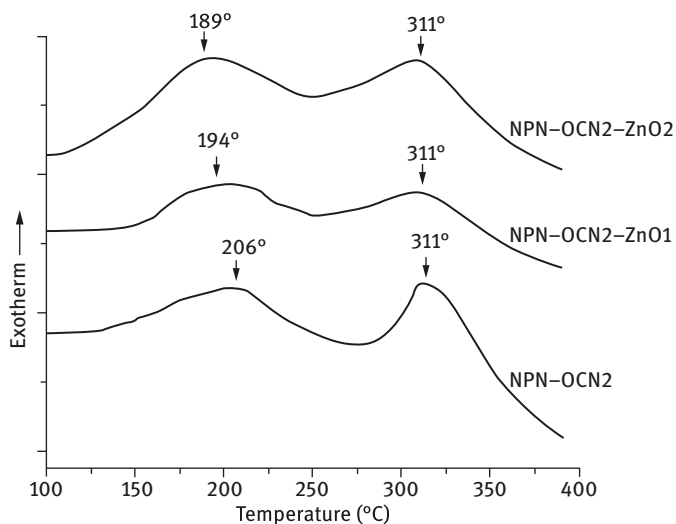
Figure 4.6: DSC scans of neat and catalysed NPN−OCN2. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *RSC Advances*, 2015, 5, 111, 91254. ©2015, Royal Society of Chemistry [36].
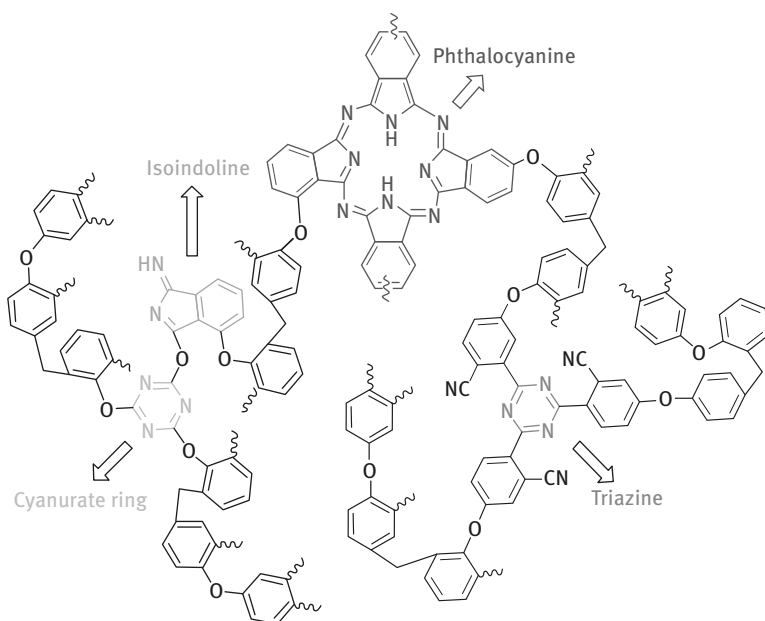
Scheme 4.15: Postulated-cured network structure of cyanate−PN resin. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *RSC Advances*, 2015, 5, 111, 91254. ©2015, Royal Society of Chemistry [36].

presence helped achieve early gelation of the resin at lower temperature as these groups are prone to be catalysed by a host of materials. Cyanation of PN polymer precursors marginally impaired the water repellent nature of PN systems and their overall thermal stability. Cyanate ester polymers are more susceptible to thermal dissociation compared to PN-modified networks.

In summary, this chapter presents a series of self-curable, PN systems with various reactive functional groups such as PR, cyanate, amine and phenols. The cure pattern depends on the nature of the co-curing groups. Phenol and amine groups trigger PN curing by the formation of iminoester and amidine intermediates, which on further reactions with cyano groups result in heteroaromatic structures like triazine and phthalocyanine. Allyl groups and PR groups facilitated the PN cure reaction via phenolic intermediates involved in their rearrangement. The introduction of cyanato groups did not confer any special characteristics to the PN resin except that it helped achieve early gelation at a relatively lower temperature.

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5 Phthalonitrile blends and composites

5.1 Introduction

In structural applications, fibre-reinforced high-temperature polymer matrix composites can offer significant advantages over other conventional metals and other materials because of their low density and high specific strength. Polymer composite materials indented for applications in aerospace structural components will be exposed to prolonged, extreme service conditions of stress, time, temperature, moisture, chemical and gaseous environments in military and commercial aircraft and hypersonic reusable space vehicles [1, 2]. Therefore, the durability and reliability of materials used in aerospace components are essentially critical. It is imperative that the polymer materials for these applications possess high glass transition temperature (T_g) (at least 25 °C above the actual use temperature), good high-temperature stability and good thermomechanical profiles. Above all, a major requirement for any high-temperature polymer, regardless of its intended uses, is the ease of processability. As a thumb rule, high-temperature performance and processability do not go hand in hand. In reality, although many monomers with multi-aromatic rings in structure are inherently stable and yield polymers with high T_g, they tend to produce polymers that have poor solubility in most organic solvents, high melting or softening points and melt viscosities.

The prominent categories of polymer matrices used for fibre-reinforced composites in aerospace applications are epoxy, cyanate ester resin and polyimides (PI) [3–5]. Phthalonitrile (PN) resins are the latest entrant to this category of matrices because of their unique combination of properties such as excellent very high-temperature performance and the addition curing mechanism that ensures little or no volatile evolution during cure [6, 7].

Although PN possesses excellent high-temperature properties, the relative intractability of the resin system renders them not the material of choice for many critical applications. Copolymerisation or blending is a well-established approach for tailoring the properties/processability of polymeric materials and it is no surprise that the same methodology is adopted in improving the processability of PN too. In this chapter, the approaches for blending of PN with other thermosets and thermoplastics, properties of the resultant compositions and finally their applications in composites are also discussed.

5.2 Phthalonitrile blends and their properties

In the open literature, a few papers deal with the blending of PN with other thermosets/thermoplastics. In the forthcoming sections, approaches of blending and

co-curing of PN with epoxies, polyarylene ethers (PAE), bismaleimides (BMI), phenolic resins, polyether ether ketones (PEEK), propargyl (PR) functional compounds and so on, are discussed.

5.2.1 Blends with epoxy and phenolic compounds

Epoxy resins are a class of most commonly used thermosetting polymer. These materials have reasonable thermal and mechanical properties and exhibit excellent processability [8]. However, the high-end applications of epoxies are hampered by the low softening temperature and thermal stability. Hence, it is an object of many researchers to enhance the thermal-performance epoxy resins to render them suitable for high-end structural applications. On the contrary, as mentioned previously, PN resins are gifted with a halo of high-performance properties but are handicapped because of their intractability. The strategy of blending with epoxy resins has been resorted to by many researchers.

On introducing epoxy groups into PN systems, the cure chemistry was found to deviate from its usual pathway to form some additional networks. PN epoxy copolymerisation results in oxazoline ring formation (Scheme 5.1). With the progress in copolymerisation, infrared (IR) characteristic absorptions of the PN nitrile band at $2{,}232\,\mathrm{cm^{-1}}$ and the epoxy groups at 917 and $860\,\mathrm{cm^{-1}}$ disappeared with the appearance of a new peak at $1{,}608\,\mathrm{cm^{-1}}$ that is characteristic of oxazoline structures. The cured networks produced from binary blends comprising bisphthalonitriles (BPh) or a PN oligomer with an epoxy resin such as diglycidyl ether of bisphenol A (DGEBA) have improved properties relative to the individual polymers [9, 10]. The copolymers were superior to the epoxy systems in terms of thermal and oxidative stability, T_g, shelf-life, moisture resistance and electrical properties.
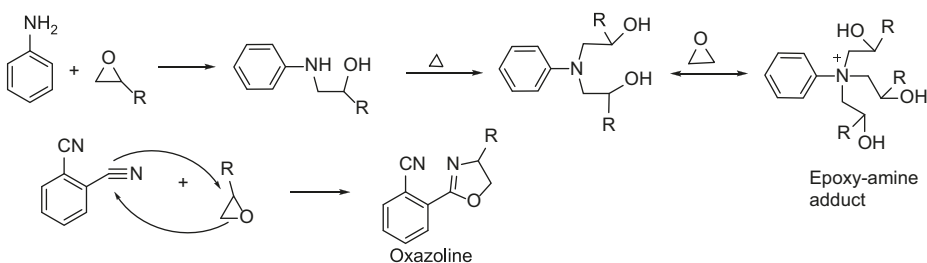
Scheme 5.1: Probable epoxy-amine and epoxy PN reactions. Reproduced with permission from D. Augustine, K.P. Vijayalakshmi, R. Sadhana, D. Mathew and C.P.R. Nair, *Polymer*, 2014, 55, 23, 6006. ©2014, Elsevier [11].

Using higher epoxides with more than two epoxy groups enhances the cross-link density of the system and increases the thermal stability of blends [12]. Thermoset blends

of 4-(aminophenoxy)phthalonitrile and epoxy resin exhibited two exothermic peaks (180–202 and 296–309 °C); the first one is due to amine-catalysed epoxy ring-opening and second is attributed to cross-linking of PN functions [13]. Spectral evidence confirmed the formation of heteroaromatic networks of phthalocyanine and triazines [14]. IR absorption peaks at 1,010 cm^{-1} indicated the NH bending vibrations of phthalocyanine ring and a band at 1,360 cm^{-1} indicated the stretching vibration of triazine ring. T_g and the initial decomposition temperature were enhanced upon increasing the PN content in the blend. At elevated temperatures, PN/epoxy blends produced a foamed protective char on the surface and this enhances the flame retardancy of epoxy systems. It also reduces moisture sensitivity of epoxy resins. 5% mass loss temperature ($T_{5\%}$) ranged from 403 to 479 °C in N$_2$ atmosphere and char yield at 1,000 °C ranged from 61 to 74% for bisphenol A (BPhA)-based blends of PN and epoxy components while $T_{5\%}$ and char yield of cured BPhA epoxy was 378 °C and 19%, respectively. Flexural strength of the composite processed from this 20:80 (PN:epoxy) blend composition increased by 40 MPa compared to pure epoxy system. However, incorporation of more of phthalocyanine resulted in brittleness, adversely affecting the mechanical properties. The rigid frameworks may be resulting from the high degree of interpenetration of molecular chains in the two phases and their higher molecular weights. A report on PN/epoxy blends realised from epoxy resin (E-44) and 2,2-*bis*[4-(3,4-dicyanophenoxy) phenyl]propane (BPhA) showed that the addition of PN groups improved flame retardancy of epoxy resins. Limiting oxygen index (LOI) value of epoxy resin showed 2% increment in blend composition with 20 wt% of PN component. UL-94 measurement showed that the burning grade was improved from no grade to V-0 grade [15].

Augustine and co-workers have studied the impact of epoxy blending on thermal stability, adhesive characteristics and morphological features of an amine-novolac phthalonitrile (APN) system [11]. Blend of APN and DGEBA manifested a multi-step cross-linking pattern. The introduction of epoxy functions into APN system altered the cure reactions from the conventional cross-linking pattern. In the case of cured amine-functionalised phthalonitrile (CAPN)/DGEBA blend, there was a significant reduction in intensity of nitrile absorption at 2,230 cm^{-1} without appreciable increase in the intensity of characteristic peaks corresponding to phthalocyanine and isoindoline moieties. This was a clear indication of nitrile curing through an alternate cure mechanism, operating via epoxy-amine and epoxy PN reactions. This made the system undergo reaction in sequences involving amine epoxy, epoxy PN and amine PN reactions (Scheme 5.1).

Since the cure reaction of DGEBA with APN is quite complex, cure behaviour of APN/DGEBA blends was investigated with the support of theoretical modelling, simulation and also by reactions employing model compounds. The feasibility of cross-linking of epoxy groups with nitrile and amine functions was theoretically modelled at B3LYP/6-31G(d,p) level of density functional thoery using aniline, glycidyl ether of *p*-cresol and 4-(4-methyl phenoxy)phthalonitrile (MPPN). The optimised structures of products of epoxy-amine and epoxy nitrile reaction pathways are presented in

Figure 5.1. The computed heat of reaction for the formation of oxazoline and epoxy-amine adduct are 150 and −96 kJ/mol, respectively and the activation barriers for their corresponding transition state are found to be 268 and 176 kJ/mol, respectively (Figure 5.2). Comparison of heat of reaction and activation energies for the two reactions suggests that reaction of glycidyl ether of *p*-cresol with MPPN or with aniline can be equally competitive and occur in the same temperature regime.
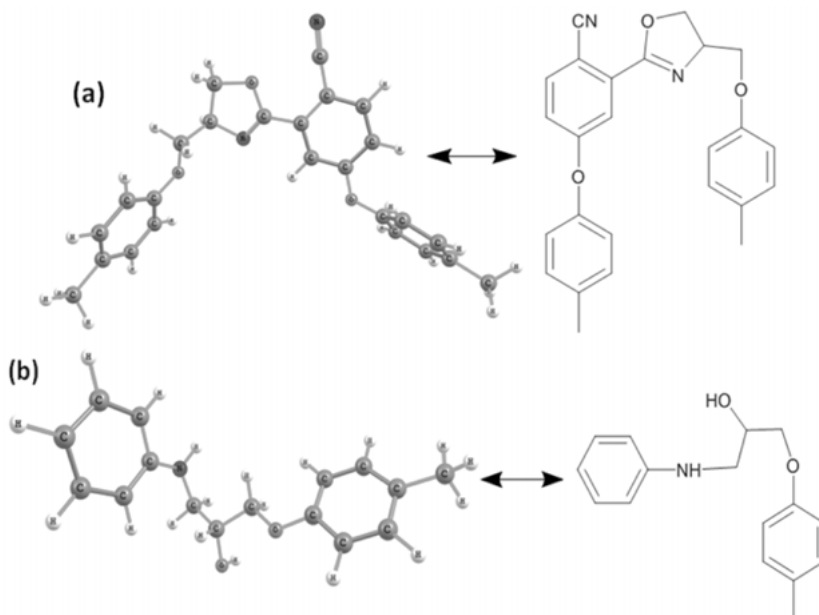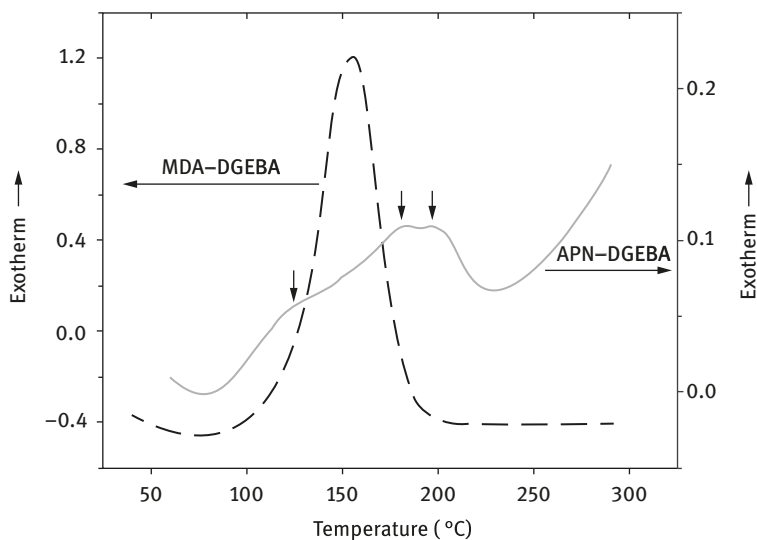

Figure 5.1: Energy minimised network structures (a) oxazoline and (b) epoxy-amine adduct. Reproduced with permission from D. Augustine, K.P. Vijayalakshmi, R. Sadhana, D. Mathew and C.P.R. Nair, *Polymer*, 2014, 55, 23, 6006. ©2014, Elsevier [11].

The reactions among PN, amine and epoxy groups were studied experimentally using MPPN, methylene dianiline (MDA) and DGEBA as model compounds. Quantitative estimation by Fourier-transform infrared (FTIR) spectroscopy was done by comparing absorption peaks of interest against the reference peak at 830 cm^{-1}, characteristic of aromatic *para*-substitution. During heat treatment at 200 °C, involvement of only about 1.5% of −CN groups was accomplished with the participation of minimal quantity of epoxy groups. Meanwhile, 44% of −CN groups were drawn into the network by the epoxy functions on heating at 230 °C with concomitant reduction in the intensities of absorption by nitrile and epoxy groups. Simultaneously, the characteristic band because of oxazoline network at 1,606 cm^{-1} got intensified with the enhancement of curing temperature. Differential scanning calorimetry (DSC) pattern also pointed toward the involvement of an alternate cure mechanism, as indicated by
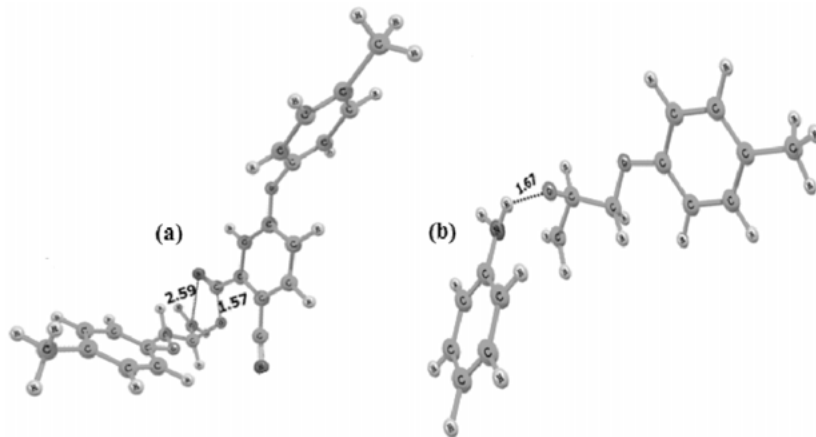
Figure 5.2: Transition state corresponding to curing of (a) MPPN/glycidyl ether of *p*-cresol and (b) glycidyl ether of *p*-cresol/aniline (bond length in A° unit). Reproduced with permission from D. Augustine, K.P. Vijayalakshmi, R. Sadhana, D. Mathew and C.P.R. Nair, *Polymer*, 2014, 55, 23, 6006. ©2014, Elsevier [11].

FTIR studies, in addition to the homopolymerisation of nitrile groups, facilitated by 1° and 2° amine groups. A separate DSC analysis (Figure 5.3) showed a broad exotherm initiating from 88 °C and extending up to 200 °C corresponding to the curing of epoxy-amine groups. DSC thermograms of APN/DGEBA blend showed a multi-step

Figure 5.3: DSC scans of APN/DGEBA and MDA/DGEBA blends. Reproduced with permission from D. Augustine, K.P. Vijayalakshmi, R. Sadhana, D. Mathew and C.P.R. Nair, *Polymer*, 2014, 55, 23, 6006. ©2014, Elsevier [11].

polymerisation reaction. Compared to APN oligomers, two additional peaks were observed for APN/DGEBA blends. The first exotherm appeared as a shoulder peak emerging at 87 °C and was because of the epoxy-amine reaction. The overlapped second and third exotherms peaked at 182 and 205 °C represented the epoxy nitrile and amine nitrile co-reactions in blend. The quantitative estimation of the extent of epoxy-amine and epoxy PN reactions in APN/DGEBA blends showed that the epoxy-amine reaction was 21% and epoxy groups available for reaction with nitrile groups was 79%. Experimental evidence corroborated by model compound studies established that the two cure exotherms in APN/DGEBA blends can be attributed to the cross-linking via epoxy PN and epoxy-amine reactions, respectively in the temperature regime of 90–230 °C. Thereafter, the reaction proceeds mainly by the secondary amine-mediated polymerisation of PN groups.

The presence of epoxy functions helped achieve early gelation at lower temperature by way of reactions of epoxy with nitrile and amine groups. The thermal polymerisation of APN resulted in stable triazine and phthalocyanine networks, whereas their blends with epoxy functional monomers resulted in epoxy-amine adduct and oxazoline structures with reduced thermal stability and char residue. In the case of APN, the initial decomposition temperatures, initial cure temperature (T_i) were all above 420 °C. About 95 wt% was retained at 500 °C and it exhibited high char yield around 78% at 900 °C. However, on blending with the epoxy resins, the temperature corresponding to 5% weight loss got reduced to 330 °C with simultaneous reduction in char residue at 900 °C to around 64%. It was observed that the thermal stability of APN got significantly decreased on blending with DGEBA. Co-cured networks formed via epoxy-amine and epoxy PN reactions are readily susceptible to thermal dissociation compared to phthalocyanine and triazine networks formed via amine PN cross-linking. APN/DGEBA blend showed 20 and 45% enhancement in lap shear strength (LSS) value at room temperature (RT) and at 150 °C when compared to neat APN. Blending with DGEBA alleviated the brittleness of the APN systems to some extent as manifested by their higher cohesive strength.

Aromatic amines are widely used as curing agents for PN/epoxy blends. These amine functionalities are more consumed in their low-temperature curing stage itself (epoxy cross-linking) and are insufficient to activate nitrile groups below 200 °C. Nitrile groups demand temperature above 300 °C for their effective cross-linking but this condition is not practically possible in the presence of relatively low and thermally stable epoxy resins. Hu and co-workers reported a binary blend composed of benzimidazole-containing phthalonitrile (PNBI)/BPhA epoxy resin E51 that showed good compatibilities and unique synergistic curing behaviours [16]. IR spectrum showed nearly full consumption of nitrile and epoxy groups for blend composition PE19 with 1:9 weight ratio of PNBI:E51 even at 150 °C. Peaks corresponding to epoxy (915 cm^{-1}) and nitrile (2,230 cm^{-1}) groups disappeared and the peak characteristic of isoindoline structures (1,630 cm^{-1}) appeared. This indicated that some highly active curing agents are generated that played an effective role in complete

conversion of nitrile functions at lower temperatures. It is assumed that initially, the imidazole moieties act as curing agents for epoxy functions and their reaction produces active intermediates such as oxygen anions. This active intermediate showed higher catalytic activity towards nitrile groups and induced PN cure reactions at low-temperature regime (Scheme 5.2). T_g of PE19-210 (PNBI/E51 blend with final cure temperature (T_f) at 210 °C for 2 h) was 207 °C. The 5% weight loss and char yield in nitrogen at 800 °C were 369 °C and 14%, respectively.
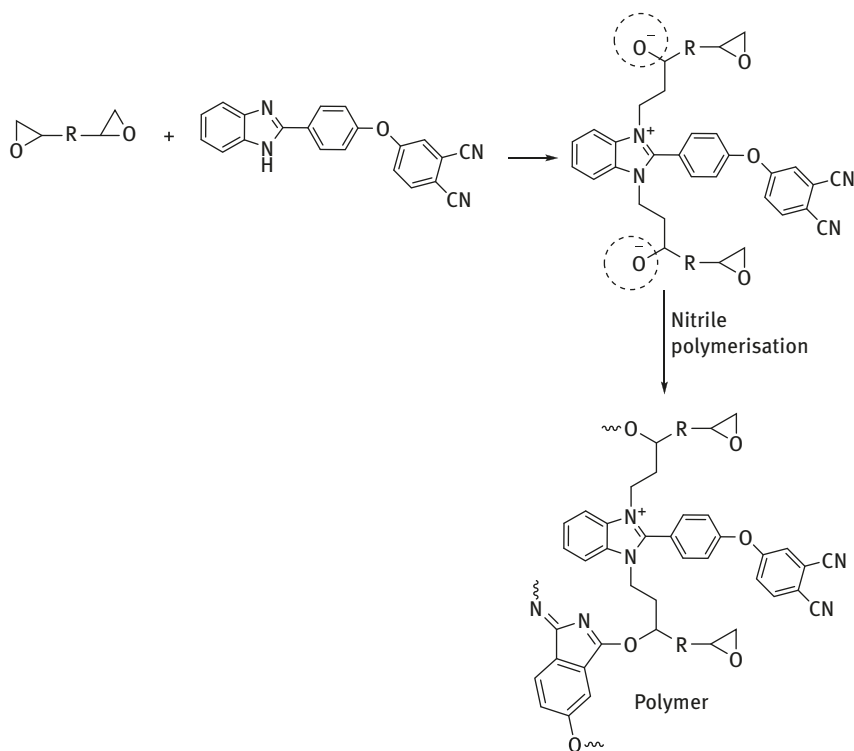
Scheme 5.2: Likely co-cure mechanism of PNBI/epoxy blends.

The nucleophilic phenol groups readily react with the nitrile groups of PN forming heteroaromatic structures such as isoindoline, triazine and phthalocyanine. Generally, novolac resins and phenolic resoles generate volatile side products in their cure reactions that eventually leads to voids and compromise the strength of their end products. Sumner and co-workers focused on this limitation of phenolic resin and demonstrated that phenolic resins cured with BPh reagent produce void-free networks with attractive structural and fire characteristics. The thermo-oxidative resistance of these networks was attributed to a high level of aromaticity and heterocyclic cross-links mainly composed of isoindoline and diimine structures [17].

In the same line, Guo and co-workers studied the self-promoted cure behaviour of blends of BPh monomer and novolac. The phenolic fractions in novolac accelerated the curing of the blends without the aid of any extra curatives (Scheme 5.3) [18, 19]. The blends had large processing windows (98–118 °C) with low melt viscosity. The processing window depended on the BPhA content. The blends exhibited tan δ peak around 100–150 °C because of novolac structure and that due to the copolymer increase up to 330 °C with increase in BPhA content to 50 wt%. On further increasing the BPhA amount, T_g was not observed up to 350 °C. Highly aromatic nature of the network imparted excellent thermo-oxidative stability, with $T_{5\%}$ at 502 °C in air for 20:80 novolac/BPhA blend. The copolymers displayed good flexural strength (49.0–91.4 MPa) and flexural modulus (4.01–5.78 GPa) depending upon the BPhA content.
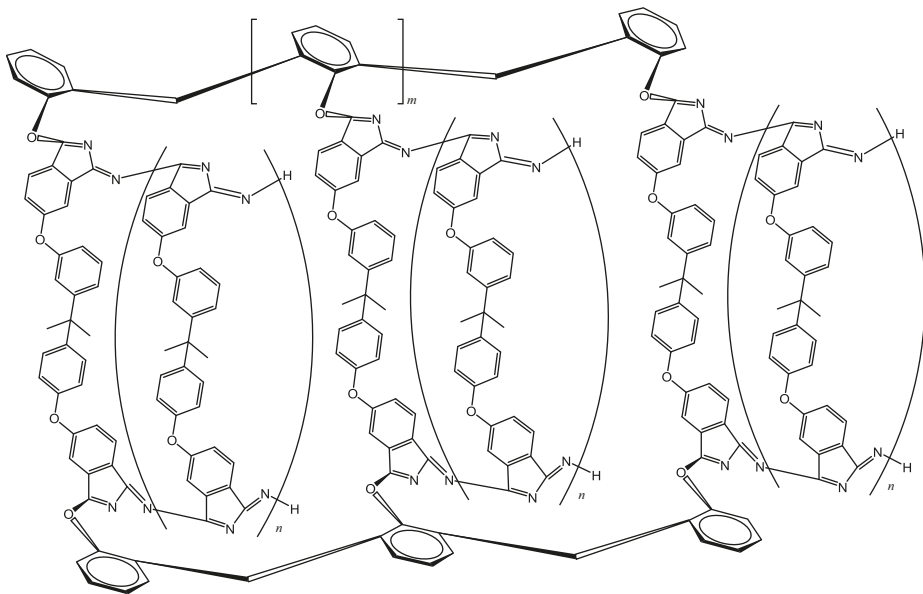
Scheme 5.3: Cured network structure of novolac/BPhA copolymers. Adapted from H. Guo, Y. Lei, X. Zhao, X. Yang, R. Zhao and X. Liu, *Journal of Applied Polymer Science*, 2012, 125, 649 [18].

5.2.2 Propargyl phthalonitrile networks

The possibility of PR groups as cure aid for PN functions have been explored by Augustine and co-workers [20, 21]. Toward this, the feasibility of co-reaction between PR and nitrile groups leading to intercross-linked heterocyclic networks via in situ-generated functional groups was investigated. The influence of PR groups on PN curing was studied through reactions of bisphthalonitrile ether of bisphenol A

(BPhAPN) and bispropargyl ether of bisphenol A (BPhPR)-based blends and simple model compounds, MPPN and 3-(4-methyl phenoxy)propyne. Blend of monomers and model compounds are abbreviated as BPhPN-PR and MPPN-PR, respectively and their cured form as cured BPhPN-PR and cured MPPN-PR. From the FTIR spectra of cured blends of model compounds, cured MPPN-PR and monomers cured BPhPN-PR (Figure 5.4) showed complete disappearance of acetylenic bond as indicated by the absence of $-C{\equiv}H$ (3,290 cm^{-1}) and $C{\equiv}C$ (2,120 cm^{-1}) characteristic absorptions and exhibited a broad peak centred around 3,400 cm^{-1} with considerable decrease in the nitrile peak intensity. Characteristic absorptions of triazine (1,560 and 1,360 cm^{-1}), isoindoline (3,300 and 1,660 cm^{-1}) and phthalocyanine (1,010 cm^{-1}) structures were also observed. These spectral changes indicated co-reaction between PR and PN groups. DSC studies also revealed a multi-stage curing pattern (Figure 5.5). Thermal cyclisation of PR ether involves intermediates, particularly the enol state and final chromene units. Both phenolic and chromene fractions can accelerate nitrile cure reaction. Thermograms of the blends showed two well-resolved endothermic transitions corresponding to the melting of the two monomers (BPhPR and BPhAPN) and an overlapped exotherm with two maxima peaked around 280 and 310 °C. The first exotherm is in the same temperature range as that of BPhPR and was attributed to the Claisen rearrangement and self-curing of PR groups in the blend, yielding chromene networks. The overlapping high-temperature exotherm with peak temperature (T_p) at around 310 °C was not present originally in either of the thermograms of the
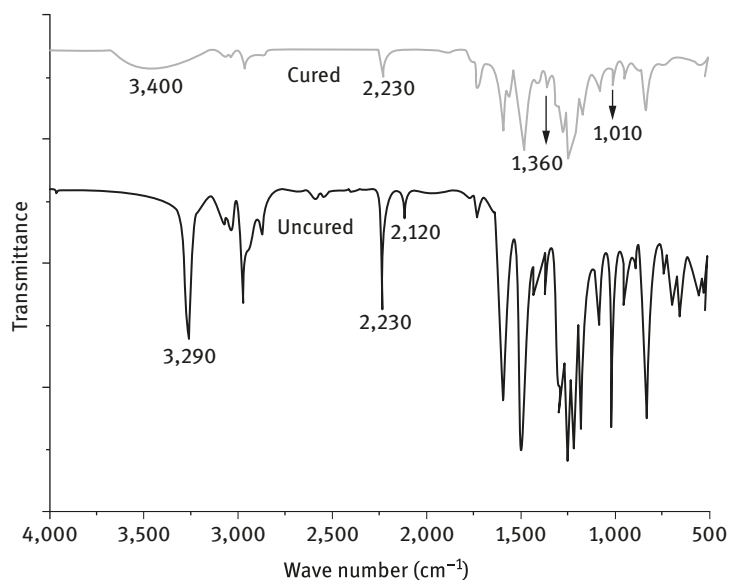
Figure 5.4: Typical FTIR spectra of BPhPN-PR and its cured form. Reproduced with permission from A. Dhanya, M. Dona and C.P.R. Nair, *Polymer*, 2015, 60, 308. ©2015, Elsevier [20].
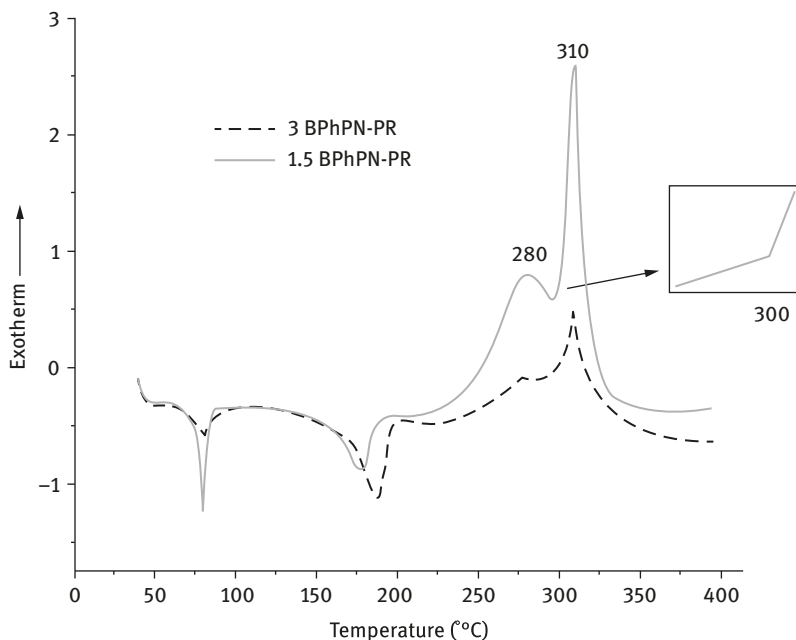
Figure 5.5: DSC scans of bispropargyl/BPh blends. Reproduced with permission from A. Dhanya, M. Dona and C.P.R. Nair, *Polymer*, 2015, 60, 308. ©2015, Elsevier [20].

monomers. This can be attributed to polymerisation of nitrile groups triggered by the chromene units. A close examination of the DSC curve revealed a discontinuity at around 290 °C (enlarged portion in Figure 5.8(b)), which can be assigned to the nitrile polymerisation facilitated by hydroxyl functions generated in the polymerisation step/secondary reactions of PR ethers. The thermal properties of monomers and blends are compiled in Table 5.1. A comparison of experimental enthalpy of cure (ΔH_{exp}) and theoretical enthalpy of cure (ΔH_{theo}) calculated from the enthalpies of homopolymerisation and composition of the blends show that on blending and curing, the heat of polymerisation is more than that expected from the respective heat of polymerisation of the individual components. This clearly shows the possibility of co-reaction between the two monomers or some catalytic nature of the cure reaction. The overall reaction leading to PN curing is shown in Scheme 4.14.

By the disappearance of chemical shift characteristic of C≡CH in 75–80 ppm range in the solid state ^{13}C-cross-polarisation/magic-angle spinning (CP/MAS) spectra (Figure 5.6) of cured blend of BPhPN-PR and comparison to their respective monomers confirmed that the PR groups have completely entered into the co-cured network. The nitrile signal at 115 ppm was unresolved due to overlap of peaks. The signal at 105 ppm of BPhAPN disappeared on curing with PR groups. Further, the absence of characteristic absorption of −OCH$_2$ at 55 ppm in the cured network

Table 5.1: Thermal properties of monomers and blends.

Monomer/ blends	Composition phthalonitrile: propargyl	T_i (°C)	T_{p1} (°C)	T_{p2} (°C)	T_f (°C)	ΔH_{exp} (kJ /mol)	ΔH_{theo} (kJ /mol)
BPhPR	0:1	195	279	–	336	400	–
1BPhPN-PR	1:1	214	281	310	341	235	200
1.5BPhPN-PR	1.5:1	218	281	310	345	214	160
3BPhPN-PR	3:1	221	282	310	392	125	100
5.7BPhPN-PR	5.7:1	230	282	310	394	79	60
BPhAPN	1:0	–	–	–	–	0	–

T_i: Initial temperature; T_{p1}: first peak temperature; T_{p2}: second peak temperature; T_f: final temperature; ΔH_{exp}: experimental enthalpy of cure; ΔH_{theo}: theoretical enthalpy of cure.
Reproduced with permission from Dhanya A, Dona M, C.P.R Nair, *Polymer*, 2015, 60, 308–317 [20].
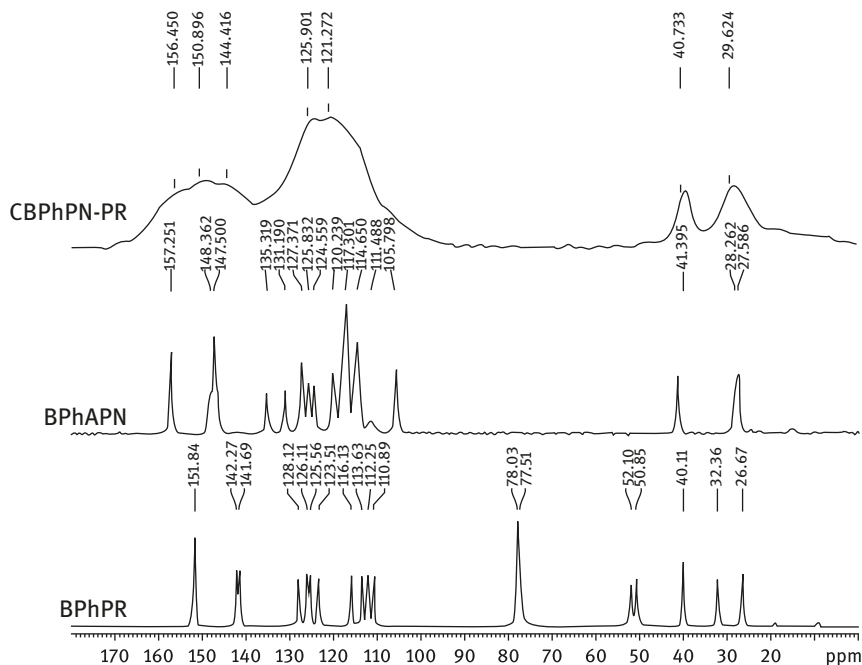
Figure 5.6: Solid-state ^{13}C-CP/MAS spectra of cured-blend cured BPhPN-PR. Reproduced with permission from A. Dhanya, M. Dona and C.P.R. Nair, *Polymer*, 2015, 60, 308. ©2015, Elsevier [20].

showed that the product formed from phenyl PR ether cyclisation is more likely to induce the –CN curing rather than chromene undergoing homopolymerisation as shown in Scheme 5.4.
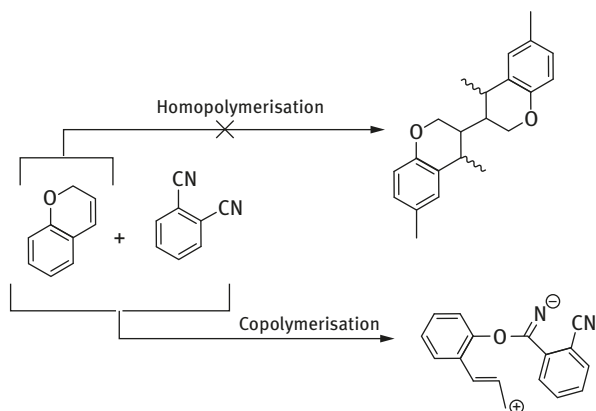
Scheme 5.4: Chromene-induced PN reaction.

All compositions of the cured PN/PR ether blends were thermally stable up to 400 °C with peak decomposition temperature around 450 °C. The thermal stability of the cured polymers may be attributed to the combined contribution of homopolymerisation and copolymerisation products in the cured networks.

5.2.3 Blends/copolymerisation with bismaleimides

Generally, to improve the properties of BMI-based resins, they are copolymerised with compound-containing allyl groups [22–24]. Zou and co-workers synthesised bisphthalonitrile monomer-containing allyl groups (DBPA-Ph) and was copolymerised with BMI in order to improve their curing behaviour. Networks formed from allyl and imide groups can maintain thermal stability of PN resins. The curing process of DBPA-Ph/BMI system involves the Ene reaction between allyl and maleimide groups, the homopolymerisation of BMI, the addition polymerisation of allyl groups and cyclisation of nitrile groups. On heating, FTIR absorption band at 1,175 cm^{-1} due to C–N–C (succinimide type) increased while C=C peak of maleimide (827 cm^{-1}) and allyl peaks at 1,630 cm^{-1} decreased. Two-stage thermal polymerisation was observed at around 263 and 332 °C. The first polymerisation step included Ene reaction between DBPA-Ph and BMI, the homopolymerisation of BMI and polymerisation of allyl moieties. The second polymerisation was attributed to the nitrile polymerisation catalysed by the active hydrogen from allyl polymerisation step. The complex cure reaction pathways involved is depicted in Scheme 5.5. T_g of DBPA-Ph/BMI copolymer was above 350 °C.

The same group that studied the cure behaviour of phthalonitrile-containing benzoxazine (BA-Ph) attempted to realise high-temperature-resistant polymers by copolymerisation of BA-Ph with BMI [25]. The first stage of the cure reaction
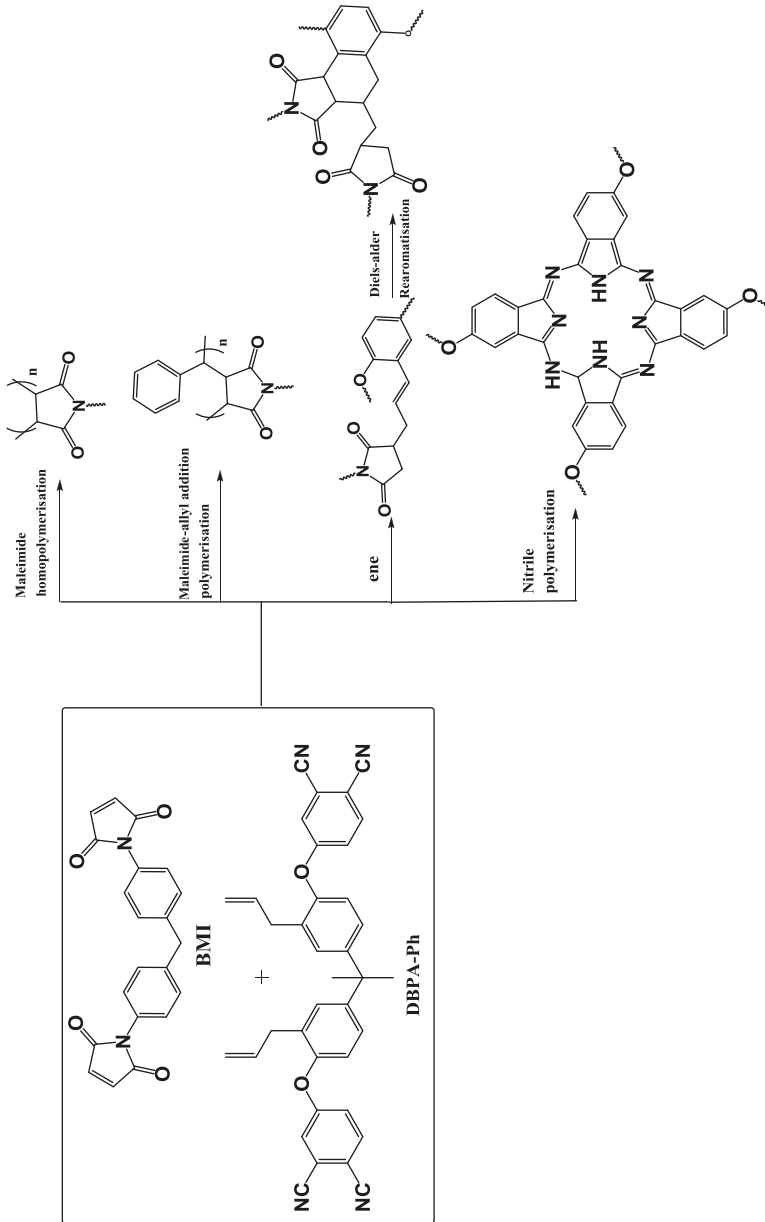
Scheme 5.5: Curing of BMI with PN.

involved mainly two reactions: (1) the ring-opening polymerisation of benzoxazine forming an arylamine Mannich bridge structure with free phenolic groups (T_p = 220–228 °C) and (2) addition reaction of these free hydroxyl with maleimide groups (T_p = 280–300 °C). The second stage comprised polymerisation of nitrile groups. With the increase in BMI content, the T_i shifted to lower side and the peaks assigned to the polymerisation of nitrile groups shifted to higher temperature. The election-deficient unsaturation in BMI cannot obviously induce nitrile polymerisation but surplus −OH functions available after the first stage of cure reaction can be utilised for nitrile reaction. The processing time and polymerisation rate of BA-Ph/BMI systems can be easily controlled by varying the processing temperature, and the proper processing temperature for BA-Ph/BMI blend was about 170 °C. They exhibited good thermal stability ($T_{5\%}$ >400 °C). Polymerisation of nitrile groups contribute to increased cross-linking that eased the stress transfer from the matrix into the fibres, leading to a higher tensile and flexural strength of their glass fibre (GF)-reinforced composites.

5.2.4 Poly (arylene ether nitrile) – phthalonitrile networks

Poly(arylene ether nitriles) (PEN) are well-known class of engineering thermoplastics having excellent combination of properties [26]. The outstanding properties arise from the unique characteristics as the aromatic portion of the PAE contribute to thermal stability and good mechanical properties of the polymer. The ether linkages are considered to facilitate polymer processing while maintaining oxidative and thermal stability. However, the high melt viscosity limited their use in composites. There have been some attempts to combine the properties of PEN with PN to derive high-performing polymer matrices.

In view of the their structural similarity (Scheme 5.6) with PN prepolymers, a lot of research works has been carried out on PEN and their blends and composites [27]. They can be cross-linked by the catalytic trimerisation of nitriles to thermally stable triazine rings. These polymers would melt at a temperature around 200 °C and flow easily and adhere to GFs. No catalyst is required for the trimerisation of the nitrile groups [28]. On blending flexible PN oligomer (n = 2)-containing biphenyl ether nitrile (2PEN-BPh) with BPh monomers, it was observed that as the proportion
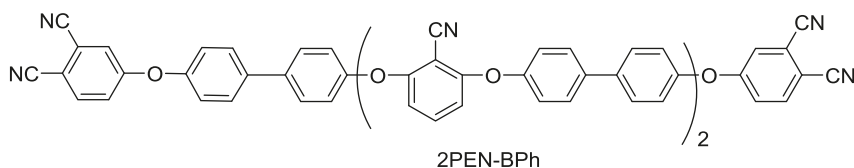
Scheme 5.6: Phthalonitrile end-capped polyether nitrile.

of 2PEN-BPh increased, the effective concentration of cyano groups in the material decreased that led to reduction in cross-link density. All the 2PEN-BPh/BPh polymers exhibited thermal stability above 550 °C and an impressive anaerobic char yield up to 78% at 800 °C [29, 30].

The average tensile strength and Young's modulus of an acid-containing co-PAE nitrile PEN-COOH were typically 83 MPa and 2.9 GPa, respectively, whereas those of PAE nitriles with pendant phthalonitrile groups (PEN-CN) were marginally higher (89.7 MPa and 3.5 GPa) [31, 32] (Scheme 5.7).
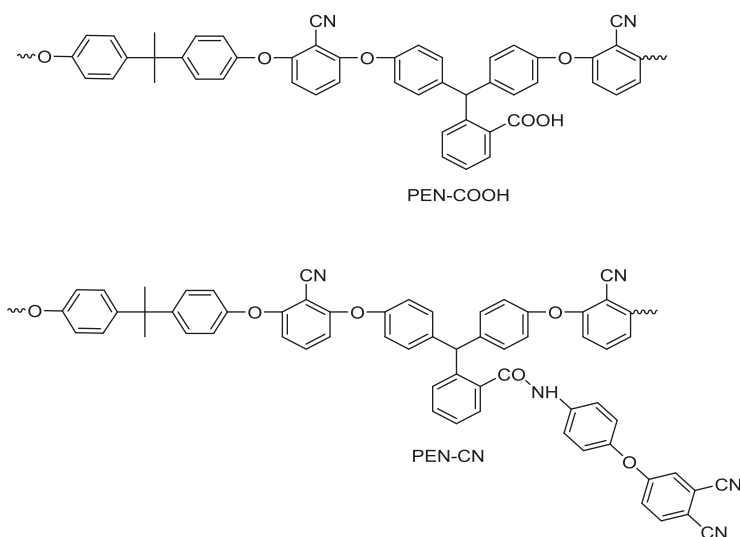
PEN-COOH

PEN-CN

Scheme 5.7: Structures of (a) PEN-COOH and (b) PEN-CN.

As a result of cross-linking in PEN-CN, the T_g improved from 182 °C to 213 °C, dielectric constant from 3.1 to 3.9 while dielectric loss (tan δ) suffered a diminution from 0.090 to 0.013 at 1 kHz – water absorption was <1 wt%. This study was extrapolated to investigate the effect of addition of PEN to phthalonitrile epoxy copolymers (BPhA/epoxy) and their GF-laminated composites [33–35]. PEN accelerated the cross-linking reaction between the PN and epoxy and initial decomposition temperature of their cured network was above 350 °C. Mechanical properties of the blends and composites showed that, flexural strength and the flexural strain increased upto 10 wt% of PEN and then decreased with further addition of PEN. These results can be ascribed to the synergistic effect between flexible PEN chains and the rigid frame of BPhA. Further introduction of flexible PEN chains (beyond 10%) into the system tended to soften-up to some extent and adversely influenced the synergism between BPhA and PEN that was manifested by the decline in their modulus values.

5.2.5 Polyether ether ketone-incorporated phthalonitrile networks

Augustine and co-workers studied the feasibility of toughening of the novolac phthalonitrile (NPN) resin using chemically modified PEEK [36]. For this, PN derivative of polyether ether ketone (PEEKPN) was synthesised by nucleophilic displacement of the nitro groups by the phenolate end functions of hydroxyl-terminated polyether ether ketone (PEEKOH) as shown in Scheme 5.8.
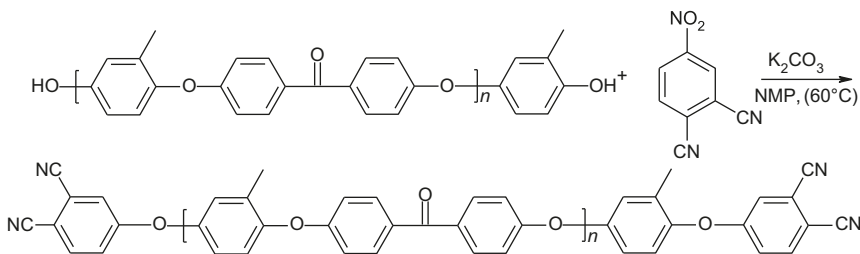
Scheme 5.8: Synthesis of PEEKPN. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *Polymer International*, 2015, 64, 146. ©2015, John Wiley & Sons [36].

The PN incorporation was confirmed from FTIR and NMR analyses, and the degree of PN substitution (extent of phthalonitrilation = 88%, functionality = 1.76) was confirmed from hydroxyl value analysis. It was observed that PEEKOH additive was capable of reducing the cure temperature of the NPN resin as in the case of blends of NPN with PEEKPN, the cure reaction is promoted mostly by the amine functionalities that was separately added as a curing agent. In the same study, when PEEKOH was blended with the system, free phenolic moieties of PEEKOH also assist the −CN reactions as shown in Scheme 5.9. However, when the PEEKOH content was increased from 10 to 30 wt%, the enthalpy of cure of first exotherm diminished from 70 to 34 J/g. An increased concentration of PEEKOH in the blend reduced the proximity of cross-linking functionalities and reduced the effective access of catalysing groups (−NH$_2$ or −OH) to the cross-linking sites. The overall cured network structure can be depicted as shown in Scheme 5.10.

Cured NPN, NPN-PEEKOH and NPN-PEEKPN were thermally stable up to 400 °C. $T_{5\%}$ and wt % retention at high temperature (68% for NPN and 71% for blends at 900 °C) got marginally improved in the blends compared to NPN system. It is noteworthy that, blending with PEEKOH facilitated the curing of the PN functions and resulted in cured networks with no loss on thermal stability and with marginally increased char residue. It was observed that mechanical properties of the carbon fibre (CF)-reinforced composites were also improved by the addition of PEEKPN which is discussed in the coming section (composite part Section 5.3).
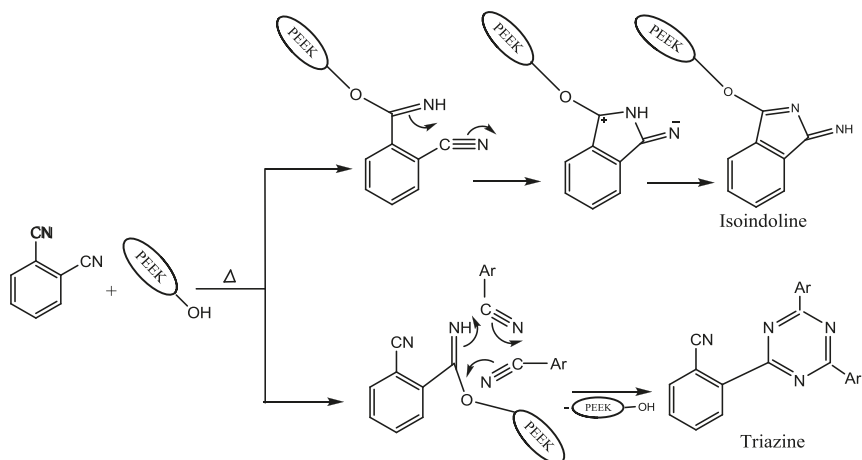
Scheme 5.9: Phenol end-functionalised PEEK (PEEKOH)-mediated nitrile curing. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *Polymer International*, 2015, 64, 146. ©2015, John Wiley & Sons [36].

In another study [11], the alterations in the cure behaviour and thermal properties of APN system by the introduction of epoxy functions were investigated by blending APN with DGEBA. APN/DGEBA blend manifested multi-step cross-linking pattern that was validated using model compounds composed of aniline, glycidyl ether of *p*-cresol and MPPN. PEEK polymer chains were introduced to the APN systems as a means to alleviate the brittleness of the cured systems. Overall cured network structures of APN/epoxy blends composed of epoxy-amine adduct, oxazoline derivatives from epoxy PN curing (Scheme 5.11) and heterocyclic intermediates resulting from amine PN cross-linking. Toughening by PEEK did not have any adverse effect on the thermal properties.

Morphological features of the CAPN, cured blends of APN/DGEBA and APN/DGEBA/PEEK are displayed in Figure 5.7. CAPN showed a rough surface with blister-like appearances, which was attributed to a brittle matrix, a trait of PN polymers. CAPN/DGEBA blend micrograph clearly depicts a smooth surface with a two-phase morphological texture where, the dispersed phases (droplets) represent the epoxy component. Interestingly, on blending further with PEEK, phase separation increased to a significant extent. The blister-like appearances on the surface were almost absent for the PEEK-blended systems, apparently indicating a toughening effect. Blending with DGEBA enabled alleviating the brittleness of the APN systems to some extent as manifested by their higher cohesive strength. The APN/DGEBA blend showed 20 and 45% enhancement in LSS value at RT and 150 °C compared to neat APN. Addition of PEEK further increased the LSS value by 45 and 81%, respectively at RT and 150 °C mainly due to the increased toughness of the cured network (Figure 5.8).
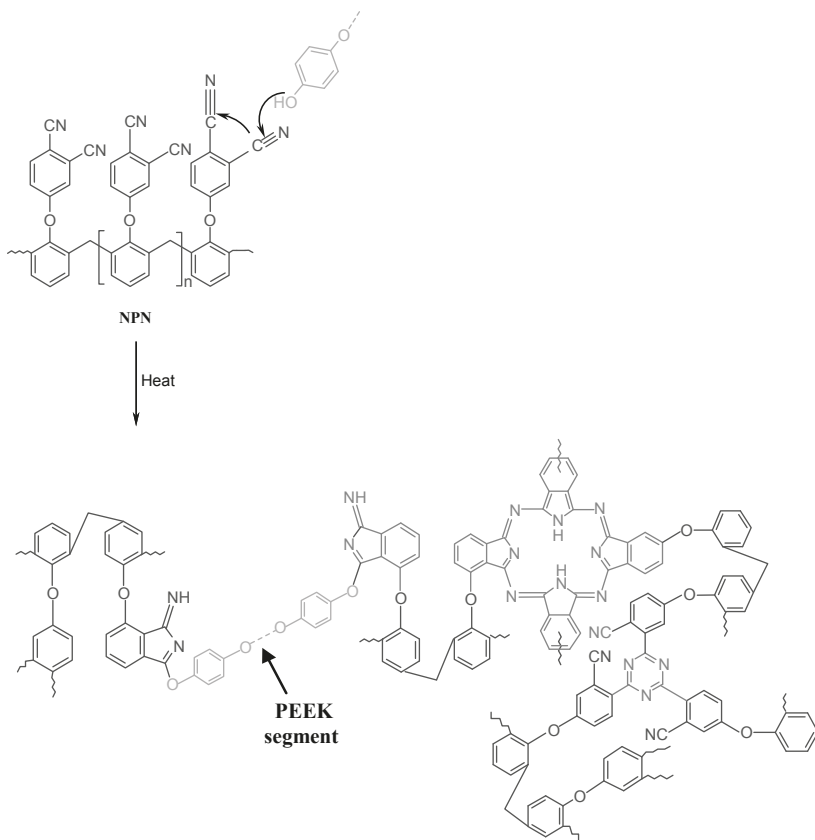
Scheme 5.10: Cured network structure of NPN-PEEKOH/PEEKPN blends. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *Polymer International*, 2015, 64, 146. ©2015, John Wiley & Sons [36].

5.3 Phthalonitrile resin-based composites

Base line comparisons with the present commercial high-temperature PI systems such as AVIMID®-N and polymerisation of monomeric reactant (PMR)-15 shows that PN polymers are more resistant to oxidative attack, making them highly attractive matrix resins for structural and thermo-structural aerospace applications. Excellent flame retardancy (equivalent to that of polybenzimidazoles[PBI]) is an added advantage of these systems with longer time-to-ignition (T_{IG}) compared to corresponding BMI or epoxy systems (~30% longer). In addition, these polymers also have a low affinity for water, which makes them ideal candidates for composites with low outgassing properties for electronic applications.

The T_{IG} of the common composites are shown in Figure 5.9 in which the high-performing polymer matrix resin systems particularly the PN and cyanate ester-
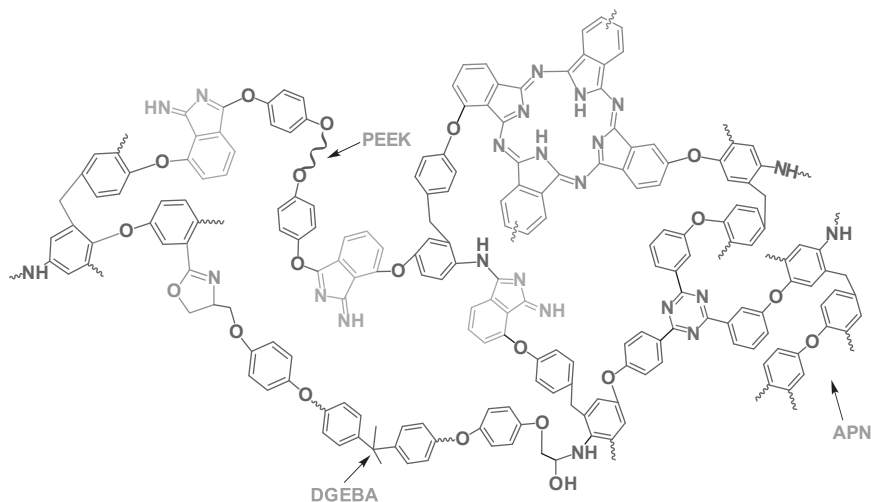
Scheme 5.11: Probable cured network structure of APN/epoxy/PEEK blends. Reproduced with permission from D. Augustine, K.P. Vijayalakshmi, R. Sadhana, D. Mathew and C.P.R. Nair, *Polymer*, 2014, 55, 23, 6006. ©2014, Elsevier [11].

based materials have much longer T_{IG}. The excellent ignition resistance of these materials is attributed to several factors, most importantly high thermal stability and low rate of release of flammable volatiles because the resins yield a high amount of char during decomposition [37].

The heat release rate (HRR) is one of the most important fire reaction properties of the composites as the heat released by a burning material can provide the additional thermal energy required for the growth and spread of fire and several other reaction properties, such as surface spread of flame, smoke generation and CO emission, are dependent on or related to the HRR. The peak HRR occurs over a very short period of time and often shortly after ignition, and is usually a good indication of the maximum flammability of a material. Figure 5.10 shows the effect of increasing heat flux on the peak HRR values for a variety of glass/thermoset laminates. It is evident that the heat released by a highly flammable composite material (i.e., glass/epoxy) rises rapidly with heat flux due to increase in the decomposition reaction rate and yield of combustibles. In comparison, the amount of heat released by high-performance thermoset composites (e.g., phenolic, cyanate ester and PN) is much lower at all heat flux levels and, in fact, the heat released by these polymers is just a small fraction of that released by the epoxy-based laminate [38].

In a study conducted by Naval Surface Warfare Centre [39], Carderock Division USA, had aggressively evaluated the fire performance of conventional and advanced glass- and graphite-reinforced composite materials. Table 5.2 show the
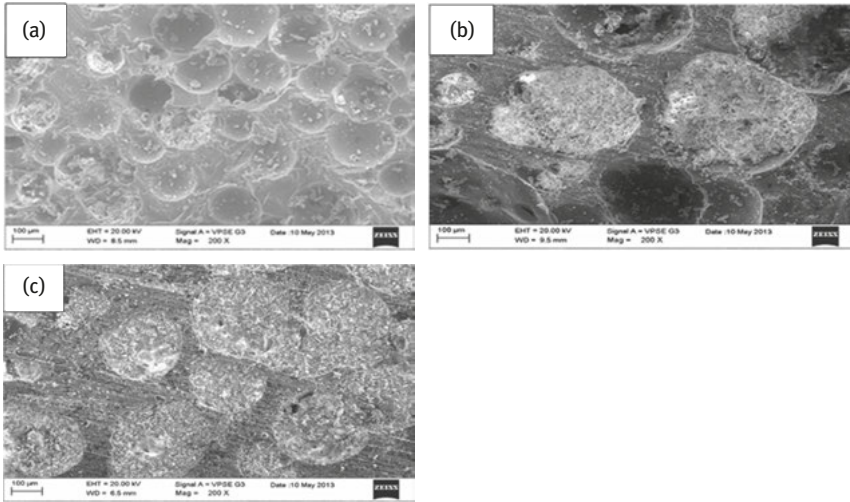
Figure 5.7: Scanning electron microscopy (SEM) micrographs of cured samples of (a) CAPN, (b) CAPN/DGEBA and (c) CAPN/DGEBA/PEEK. Reproduced with permission from D. Augustine, K.P. Vijayalakshmi, R. Sadhana, D. Mathew and C.P.R. Nair, *Polymer*, 2014, 55, 23, 6006. ©2014, Elsevier [11].
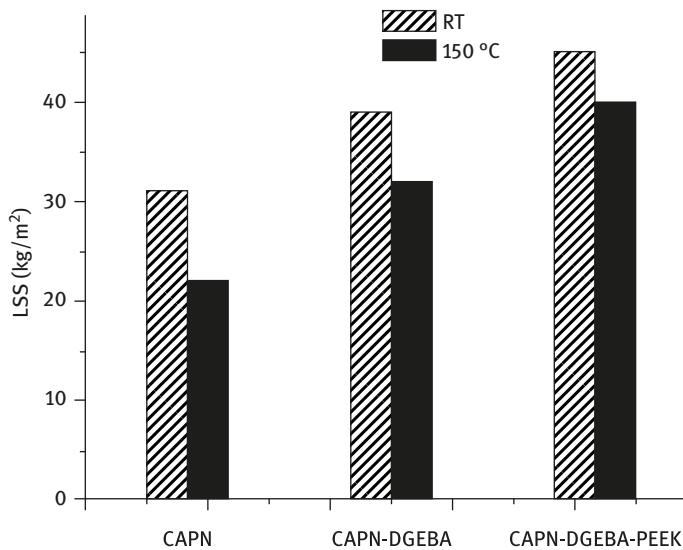
Figure 5.8: LSS bond versus composition of polymer. Reproduced with permission from D. Augustine, K.P. Vijayalakshmi, R. Sadhana, D. Mathew and C.P.R. Nair, *Polymer*, 2014, 55, 23, 6006. ©2014, Elsevier [11].
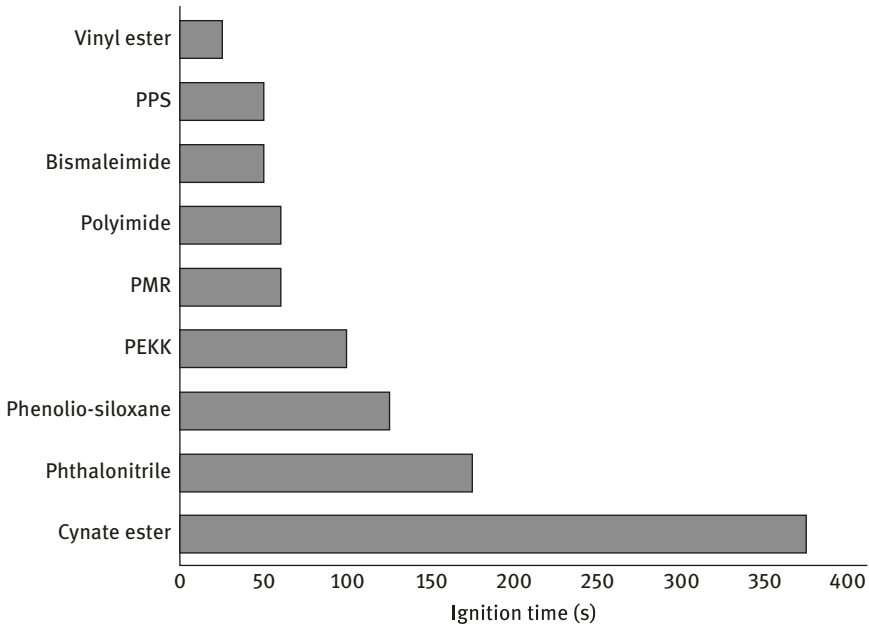
Figure 5.9: The T_{IG} of the common composites (PEKK: polyether ketone ketone and PPS: polyphenylene sulfide). Adapted from N.A. Dembsey and D.J. Jacoby, *Fire and Materials*, 2000, 24, 91 [37].
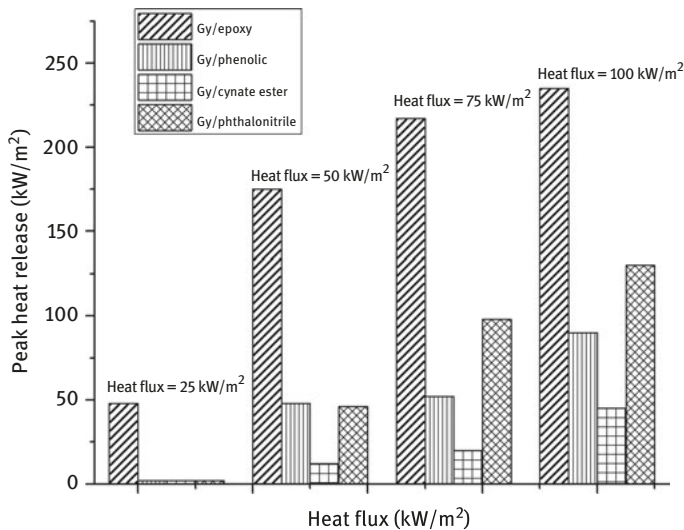
Figure 5.10: Effect of heat flux on the peak HRR values for various glass/thermoset laminates. Adapted from A.P. Mouritz and A.G. Gibson in *Fire Properties of Polymer Composite Materials*, Springer Science & Business Media, New York, NY, USA, 2007 [39].

Table 5.2: Summary of heat release data for polymer composites at heat flux (100 kW/m^2).

| | Time to ignition (s) | | Peak heat release (kW/m^2) | |
| | MlL-STD-2031 (60 s) | | MlL-STD-2031 (150 kW/m^2) | |
Composite	Carbon	Glass	Carbon	Glass
Phthalonitrile	75	59	118	106
Vinyl ester	–	24	–	187
Epoxy	28	40	232	232
Bismaleimide	22	38	270	285
Phenolic	25	25	96	133
Polyimide	55 (PMR-15)	55	85 (PMR-15)	85

T_{IG} and peak HRR of the selected conventional and advanced fibre-reinforced composite materials. The thermoset materials evaluated were vinyl esters, epoxies, BMI, phenolics and PI. The thermoplastic materials evaluated included PPS, PEEK, polyether sulfone, polyaryl sulfone, PEKK, silicone and PN. The data showed that except PN composites, most of the commercially available unprotected composite material systems did not meet the MIL-STD-2031 ignitability (T_{IG}) requirements of 60 s at a heat flux of 100 kW/m^2. When compared to the state-of-the-art high-temperature-resistant thermosets and thermoplastics, PN polymers have a very low heat release capacity.

Fibre-reinforced composites utilising high-temperature polymers are more resistant to ignition but can suffer from poor processing characteristics and mechanical properties. The increased usage of polymers and composites by the industry will demand materials with better fire performance, structural integrity and ease of processability [40]. For any composite fabrication, the processability of the matrix resin is an important parameter as it determines the widespread utility of the polymer matrix. This processability aspect of PN has been investigated widely. B-staging of PN can be performed typically by adding catalytic amounts of curing agents (1.5–2 wt%, typically diamines) into molten PN monomers and rapidly cooling to RT. It has been reported that the B-staged PN can be used for solution or melt prepregging and stored under ambient conditions for a long time [41, 42]. Zeng and co-workers [43] compiled the important characteristics of PN related to processing as follows:

1. PN monomer/B-staged resin exhibited a very-low melt viscosity in the range of <0.1 Pa.s [44]. This is a welcome advantage from the processability point of view as it enables them to be processed by techniques such as resin infusion moulding, resin transfer moulding (RTM) and filament winding.
2. Like other classes of thermosets such as BMI and cyanate esters, the addition-type polymerisation mechanism of PN resins does not produce any volatiles during curing. This is extremely advantageous as low-cost composite production techniques such as RTM can be employed.

3. PN resins have low enthalpy of polymerisation unlike in the case of cyanate esters [45]. This inherent property helps them to be used for fabrication of thick composite laminates where, high quantity of resin may be required to impregnate the reinforcing fabric/fibre. The low rate of exothermic heat generation helps to alleviate sudden temperature raise and temperature gradient within the materials frequently occurring in composite processing.
4. The polymerisation rate is also easily controllable as a function of curing additive [46].

Mangalgiri [47] in an early report describes about the composite materials for aerospace applications and the merits of PN polymers as potential candidate material for the future high-performance applications. PN resins for high-temperature applications are cured in conventional manner (at 180–200 °C) but can be post-cured, albeit in inert atmosphere to the temperatures up to 600 °C. The author pointed out that, PN have better processibility, good fracture resistance, better strength and modulus and very-low moisture absorption compared with the presently available PMR resins for high-temperature (250–350 °C) applications. Sastri and co-workers [48] reported that most of their initial composite efforts have involved using aromatic diamines with ether linkages as curing additives and the amount of the same to form a PN prepolymer is limited due to the reactivity of the amine towards the monomer. After the formation of the prepolymer, upon cooling, the B-staged prepolymer was a frangible solid, which can be powdered and stored at RT for a long period. The low cure exotherm of PN polymers enabled them to be used in RTM-type composite processing techniques. Certain other prepolymerisation compositions formed from mixing various amounts of PN monomer and aromatic amine curing additive at RT were melt processable and is stable under ambient conditions before melting occurs. Upon melting, the polymerisation rate depends on the composition of the mixture and melt temperature. These compositions were especially useful for fabrication of composite components by RTM, filament winding, injection moulding or prepreg formulation from the melt in the absence of solvent. In the molten condition, the curing additive reacts with the PN monomer resulting in B-staged prepolymer. Efforts were also made to fabricate carbon–carbon composites using PN [48]. This was achieved from the CF-reinforced polymers of PN resins followed by pyrolysis to form the final carbon–carbon composites. It is reported that by this method, it is possible to make a dense, void-free composite in a single cycle involving impregnation, cure and pyrolysis other than the multiple steps of impregnation, cure and pyrolysis that are necessary with the other resin systems to achieve the acceptable density. PN-based CF composites were compared with the existing high-performance polymer composites [49]. The prepolymer exhibited a T_g ranging between 70 and 85 °C, depending on the amine concentration used, and melt only at temperatures

>230 °C. The T_g of the PN resin advanced with the extent of cure and eventually disappeared with heat treatment to 375 °C. These PN neat resins and composites exhibited mechanical properties that were either superior or comparable to the state-of-the-art high-temperature PMR-15 composites (Table 5.3). Toxic gas emissions from different thermosets are compared in Table 5.4 and Figure 5.11. The composite panels post-cured at 375 °C did not exhibit any T_g up to 450 °C and retain about 90% of their initial modulus. Their water uptake level remains less than 1% after immersion in water for 16 months and were found to be excellent flame resistant [50].

Graphite fibre (IM7) PN composites [51, 52] have retained their tensile strength to temperatures up to 538 °C, whereas epoxy-based graphite fibre-reinforced composites suffered a decline in tensile strength rapidly at temperatures around 260 °C for similar short time exposures (Figure 5.12). Comparison of normalised ultimate strength of graphite epoxy systems and graphite PN showed that the former lost nearly half its strength as early as 300 °C, whereas the PN composite showed no significant knockdown in strength until temperature reaches 500 °C. A localised transverse fracture occurred along with some longitudinal splitting in the case of graphite epoxy composites. When the temperature is 260 °C, the failure mode changed due to extensive softening of the epoxy matrix. The ability to sustain interfibre shear stresses and to remain bonded to the graphite fibre does not appear to be significantly degraded, as indicated by the retention in tensile strength.

The failure modes of these two composites showed a classic RT failure mode of a graphite epoxy (Figure 5.13(a)) in Figure 5.13, where a localised transverse fracture occurred along with some longitudinal splitting. When the temperature is 260 °C, however, the failure mode changed dramatically (Figure 5.13(b)), where the fracture process became much more diffused as a result of the extensive softening of the epoxy matrix at elevated temperatures. The graphite PN also exhibited a change in failure mode over the temperature range of 25–482 °C, as can be seen by comparing Figures 5.13(c) and Figure 5.13(d), as a result of changes in the mechanical behaviour of the PN resin system at high temperature. However, the ability to sustain interfibre shear stresses and to remain bonded to the graphite fibre does not appear to be significantly degraded, as indicated by the retention in tensile strength shown in Figure 5.12.

Another report on the CF-reinforced PN composites, panels were fabricated by prepregging method using a low volatile (up to 400 °C) *bis*[4-(4-aminophenoxy) phenyl]sulfone as the PN curing additive instead of 1,3-*bis*(3-aminophenoxy)benzene (200 °C) [53]. The new curing agent, was able to fully cured PN composites and found to have no significant effect on the RT mechanical properties of the composite. The composites retained about 70% of their RT storage modulus and apparent interlaminar shear strength when heated to 450 and 371 °C, respectively. Low viscosity PN formulation for RTM methods were prepared by combining 4,4′-

Table 5.3: Properties of phthalonitrile and PMR-15 neat resins and composites.

Property	Phthalonitrile neat resin	Phthalonitrile/IM7 unidirectional composite panel	PMR-15 neat resin	PMR-15/IM7 unidirectional composite panel
Tensile strength (MPa)	80 (±7%)	2,000 (0° tension) 41 (90° tension)	43–84	2,500 (0° tension) 29 (90° Tension)
Tensile modulus (GPa)	4.4 (±5%)	183 (0° tension) 10 (90° tension)	4	146 (0° tension) 9 (90° tension)
Elongation at break (%)	1.2 (±5%)	–	1.4–2.5	–
Flexural strength (MPa)	80 (±9%)	2,380 (0° flexure) 80 (90° flexure)	76	1,530 (0° flexure)
Flexural modulus (GPa)	4.2 (±3%)	174 (0° flexure) 11 (90° flexure)	3.2	122 (0° flexure)
Fracture toughness, G_{1c} (J/m^2)	120–130	–	87	–
Glass transition temperature (°C)	>375	–	327	–
Water uptake (% in 24 h)	0.2	–	0.4	–
Water uptake (% in 2 weeks)	0.6	–	1.6	–
Short beam shear strength, MPa (±%)	–	85 (2)	–	105 (2)

Table 5.4: Gas yields from various composites.

Composite	Hydrogen cyanide(ppm)	Hydrogen chloride(ppm)
Glass/vinyl ester	0	0
Glass/epoxy	5	0
Glass/bismaleimide	7	Trace amount
Glass/phenolic	1	1
Glass/polyimide	Trace amount	2
Glass/phthalonitrile	Trace amount	0

(1,3-phenylene bis(oxy)diphthalonitrile (RPN)) with low melting siloxane-bridged SiPhMePN and thermo-oxidatively stable phosphorus bridged PN. The composites showed retention of their mechanical properties even at 300 °C and showed remarkable flame retardancy with LOI value of 80% [54].
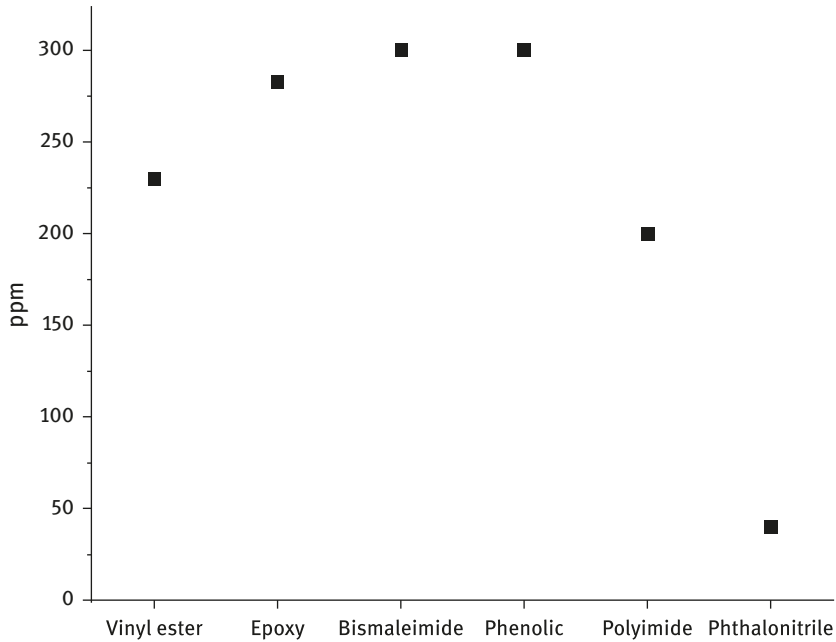
Figure 5.11: Level of CO_2 emission from glass fibre-reinforced composites. Adapted from A.P. Mouritz and A.G. Gibson in *Fire Properties of Polymer Composite Materials*, Springer Science & Business Media, New York, NY, USA, 2007 [39].
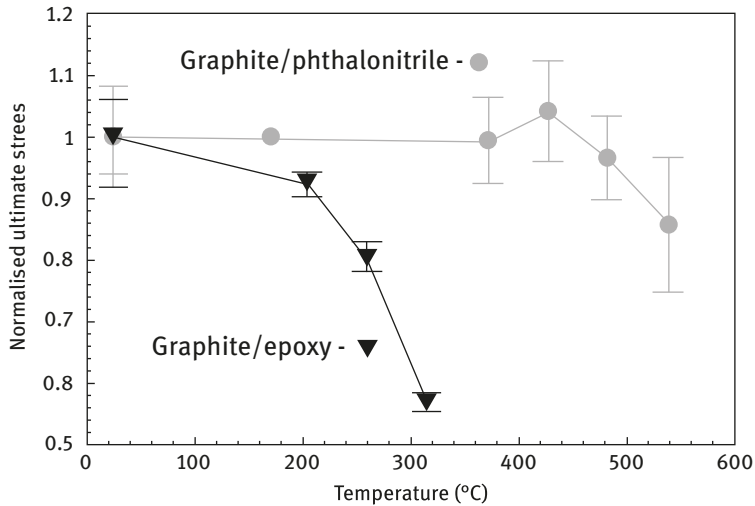
Figure 5.12: Normalised elevated temperature ultimate strengths of graphite PN and graphite epoxy systems. (Adapted from A.P. Mouritz and A.G. Gibson in *Fire Properties of Polymer Composite Materials*, Springer Science & Business Media, New York, NY, USA, 2007) [39].
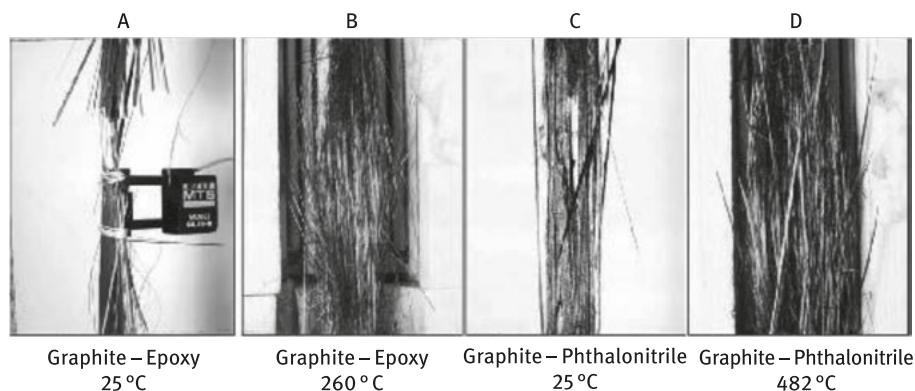
Figure 5.13: The failure mode of graphite PN and graphite epoxy composites.

Addition curable resins offer void-free components unlike the conventional condensation polymerisation systems. This advantage results in the usage of the reduced cure pressure and eliminates the need of degassing the composite during the processing and will reduce anomalies such as wedge out, ply lift sub-char ply separations and pocketing in composites. Hence, high-temperature-resistant addition curable resin systems including PN were compared for the application in solid rocket motor nozzle ablative component composites [55]. The addition curable resin systems contemplated were PN, diethynyl diphenyl methane (DEDPM), phenolic triazine (PT) and polyphosphazene (PZ) and phenolics. The thermogravimetric analysis (TGA) data showed that PN were stable up to 500 °C to initiate the onset of mass loss as presented in Table 5.5.

The ablative performance evaluation by plasma torch method for 10 s resulted in a mass loss of the PN material for 3.3 wt% when compared to the mass loss of baseline phenolic (4.2%). The results of all addition cure resin systems are summarised in Table 5.5 after subjecting to ablation test.

B-staged amorphous BPh polymers were used for fibre sizing applications [56]. The fibres were passed through an organic solution of the PN prepolymer and subsequently subjected to curing. The coated fibres were having excellent high-temperature properties when used for the fabrication of composites or prepregs. This invention is interesting as the current material used for the sizing purpose like epoxy, decompose at high temperatures of the advanced composite processing technology, which causes the composites to fail on exposure to these elevated temperatures. Metal PN composites have also been explored for acoustic applications. The composites were realised by impregnating the PN prepolymer into metal foams and subsequent curing. The resultant metal PN composite had excellent acoustic damping and structural properties along with high-temperature- and flame-resistant properties.

Table 5.5: Results after TGA and ablation test.

Properties	Phenolic triazine (PT)	Diethynyl diphenyl methane (DEDPM)	Phthalonitrile (PHTH)	Polyphosphazene (PZ)	Carbon cloth phenolic (CCP)
Char yield (wt %)	62.9	67.3	65.2	39.1	57.8
Onset of mass loss (°C)	460	590	500	500	365
Composite density (gm/cc)	1.26	2.26	1.34	1.39	1.45
Resin content, wt %	32	–	30	34	34
Material affected depth (in.)	0.76	0.77	–	0.40	0.56
Char thickness(in.)	0.43	0.53	–	0.26	0.34
Erosion rate (mile/s)	8.6	6.4	–	7.0	6.0

CF-reinforced composites with fibre-to-resin ratio (70:30) were processed using plain weave carbon fabric and NPN oligomers having varying degrees of PN (NPN-1: 44%; NPN-2: 71%; NPN-3: 87%; and NPN-4: 99 mol% PN substitution) [19]. Mechanical properties of the phenol-dominated compositions were found to be superior to the PN-dominated compositions as shown by the 50% higher compressive strength for phenol-rich NPN-1 as compared to NPN-4. Flexural strength and interlaminar shear strength also exhibited similar trend, for the given fibre–resin ratio, as shown in Figure 5.14.
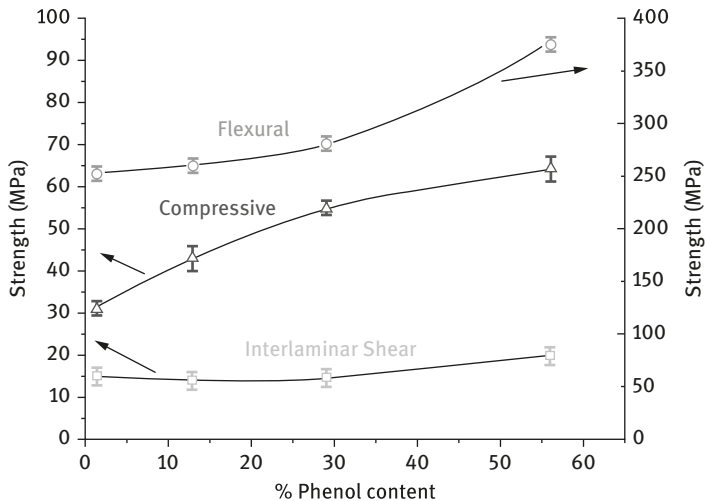
Figure 5.14: Dependency of mechanical properties of composites on polymer composition. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *Polymer International*, 2013, 62, 7, 1068. ©2013, John Wiley & Sons [19].

This trend is attributed to the better interaction of phenol-mediated matrix with the reinforcement in the phenol-rich PN composites, resulting in a stronger interphase. The −OH groups are conducive for promoting the fibre–resin interaction by way of polar interaction. The lower mechanical properties exhibited by NPN-4, in spite of the higher PN content may be due to poor interaction with the reinforcement and higher content of rigid structures in the matrix leading to matrix embrittlement. The morphological texture of composites showed that fibre wetting was poor in the case of NPN-4 and NPN-3 where the bare fibre surfaces were clearly visible. In the case of composites of NPN-1 and NPN-2, better wetting was observed since −OH groups promote fibre wetting. The failure in these cases was attributed to the fibre breakage as well as interphase failure. Formation of more polar crosslinking groups (such as isoindoline) in presence of OH groups was also responsible for consolidating the interphase leading to better mechanical properties of phenol-rich PN polymers.

Phenol-rich systems exhibited a T_g at 290 °C, whereas that of PN-rich system was above 300 °C. Further, with the increase in PN fraction in the polymer, LOI value of the composites improved systematically as seen from Figure 5.15. This is due to the formation of char at the expense of combustible volatiles, which in turn increases the oxygen levels required to sustain combustion. Though LOI increases with increase in PN composition, the increase is not significant above 70% PN content.
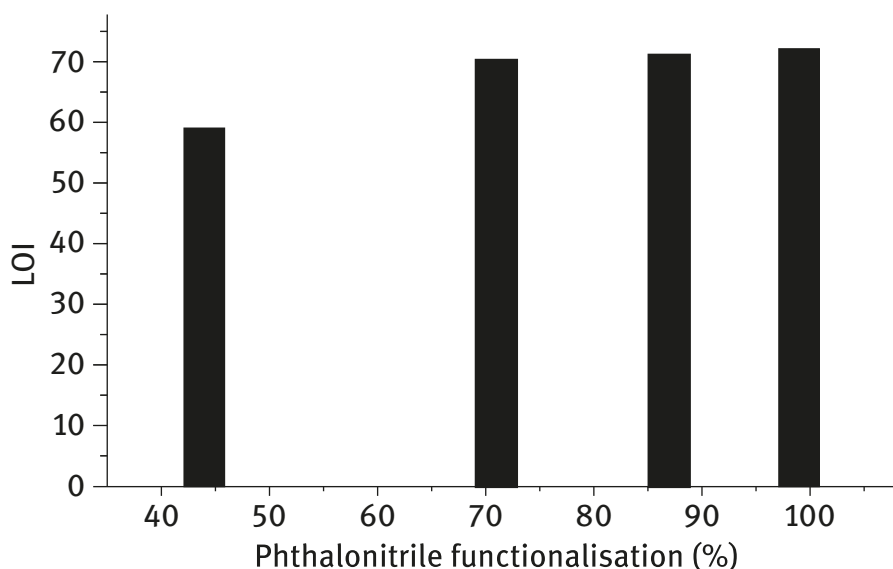
Figure 5.15: Flammability characteristics of NPN composites. Reproduced with permission from D. Augustine, D. Mathew and C.P.R. Nair, *Polymer International*, 2013, 62, 7, 1068. ©2013, John Wiley & Sons [19].

Blending with the thermoplastic backbone tends to balance the rigidity and flexibility characteristics and improves the toughness of the PN composites [36]. The influence of PEEK/PEEKPN in different compositions on NPN resin was investigated for their cure behaviour and mechanical properties of carbon fabric-reinforced composites. The inclusion of thermoplastics resulted in higher flexural strength of the composites with NPN-PEEKOH blend matrices in comparison to that of neat NPN resin. Interestingly, the mechanical properties showed a steady increase with the increase in the PEEKOH content up to 20 wt% followed by a decline in strength thereafter. Significant improvement in flexural strength (about 230%) was achieved by blending with 20 wt% of PEEKOH. However, as the PEEKOH content reached 30 wt% of the total resin, 47% reduction in flexural strength was observed compared to NPN containing 20%PEEKOH. The same trend was reflected in the case of impact strength also. Toughening by PEEKOH was confirmed from the significant increase in their resilience values. About 150% improvement in impact energy was achieved by blending with 20 wt% PEEKOH. However, further increase in PEEKOH resulted in a proportional decrease in impact energy. This indicates that the toughening mechanism was effective only up to an optimum 20% of PEEKOH beyond which, the effect in the properties is less pronounced. Area under the stress–strain curves of varying matrix compositions was maximum for 20 wt% PEEKOH loading, implying optimum toughness for this composition. However, similar improvement in mechanical properties was not observed for NPN blend with 20 wt% PEEKPN content. This implies that blending with PEEKPN was not as effective as that of PEEKOH in improving the matrix properties. This is attributed to the formation of polar heterocyclic groups such as isoindoline by way of phenol nitrile reaction in NPN-PEEKOH blends that improved the matrix-reinforcement interphase in their composites.

Fibre wetting was poor in the case of composites of neat NPN compared to the blends. Fibre pull-out and breakage were visible in NPN/carbon composites that clearly demonstrated their brittle nature. Incorporation of PEEK enhanced the fibre wetting that consolidated the interphase in a better manner and toughened the system. Better interphase was achieved at an optimum blend composition containing 20 wt% of PEEKOH beyond which a reverse trend was observed. Increasing the amount of toughening agent transforms the matrix morphology such that it was less conducive for a ductile phase. This trend was also observed in their mechanical properties. Thus, better fibre wetting and good adhesion between matrix and reinforcement were observed for blend composition with 20 wt% of PEEKOH as seen in SEM images. However, the same blend composition with 20% PEEKPN did not show such features and it could not toughen the composite to the same extent. This clearly pointed out the role of phenolic moieties in PEEK for the formation of a different cross-linked structure resulting in effective consolidation of the interphase, leading to better mechanical properties.

GF-reinforced composites of DBPA-Ph and BMI exhibited relatively better mechanical properties (>440 MPa) and satisfactory thermal properties (>440 °C). The authors report that with the increased curing temperature, the flexural strength and flexural modulus of DBPA-Ph/BMI/glass fibre (GF) composite laminates increased slightly, from 475.5 to 497.8 MPa and the flexural modulus increased from 29.2 to 33.1 GPa. This may be due to the fact that with the increasing curing temperature, the polymerisation degree of resin in composite laminate increased leading to a higher bond strength between matrix and GFs. Dielectric properties of DBPA-Ph/BMI/GF composite laminates showed that dielectric constant and dielectric loss decreased with increasing BMI content [22, 23]. Moreover, DBPA-Ph/BMI/ GF composite laminates show stable dielectric content over a wide frequency range.

5.4 Nanomaterial-modified phthalonitriles

Only a few reports are available on the effect of nanomaterial incorporation into PN polymers. Thermally stable nanocomposites comprising alternate organic (PN resins) and inorganic layers (phyllosilicates) were found to be particularly advantageous as gas barriers and flame retardant structures [57]. BPh were modified using exfoliated graphite nanoplatelets (xGnP) by RTM process [58]. xGnP/BPh prepolymer system possessed higher complex viscosity and storage modulus than the pure BPh prepolymer suggesting a profound impact of the xGnP on the cure behaviour. The thermal stability of the xGnP/BPh nanocomposite increased with increasing xGnP content. Significant improvement in mechanical properties was achieved for the nano-modified BPh matrix by effective stress transfer at the xGnP–BPh interfaces. Similarly, graphite nanosheets (GN)-reinforced PEN nanocomposites exhibited enhancement in tensile and flexural properties and improved the thermal and electrical properties of PEN owing to better adhesion of GN with PEN matrix and effective load transfer from resin to the GN [59]. PEN/BPh interpenetrating polymer network was reinforced with graphite nanoplatelets to form high-strength and high-toughness polymer networks [60]. The toughness and strength of BPh resin can be enhanced with the incorporation of PEN at the cost of modulus and thermal stability. This decline in properties can be effectively compensated by the GN incorporation.

Graphene oxide (GO) is an excellent choice as it has high density of functionalities, especially epoxy and hydroxyl functions, which can possibly favour nitrile cure reactions. Moreover, the functionalised graphene can easily be dispersed in polymers if functional groups on it interact with polymer chains to develop strong interfacial adhesion [61–63]. Functionalised graphene can catalyse the curing process by chemical interactions and affect the network formation of various thermosetting matrices [64–67]. This brings about changes in the network structure and curing dynamics of the resin, thus finally affecting the properties of the resultant networks. As reported earlier, amine groups can accelerate PN curing. Nonetheless,

only a small amount of nitrile functions became part of the cured networks. In one of our work [68], the effect of addition of GO on the curing characteristics, final network structure, thermal properties and morphology of APN were investigated. GO-bearing epoxy and hydroxyl functionalities of an empirical formula of C[O] 0.19[OH] 0.01, where [O] representing epoxide groups was explored as a curing agent for PN systems. GO revealed two major influences of GO on APN; lowering of curing temperature by about 100 °C and achievement of complete conversion of nitrile groups with accelerated cure reaction. Curing of amine-functionalised NPN in presence of GO lowered the cure temperature with complete conversion of nitrile groups and the extent of nitrile conversion with GO content is represented in Figure 5.16.
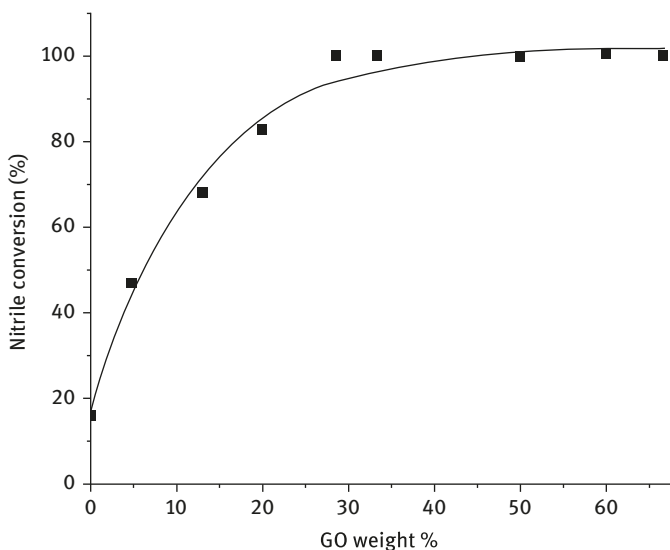
Figure 5.16: Extent of nitrile conversion with GO content. Reproduced with permission from T.M. Robert, D. Augustine, D. Mathew and C.P.R. Nair, *RSC Advances*, 2015, 5, 1198. ©2015, Royal Society of Chemistry [68].

As discussed in the case of APN/DGEBA blends [11], different possibilities of cure reaction exist in APN/GO blends too due to the multiple functionalities present in GO. Thus, APN/GO blend, rich in nitrile cure favouring multifunctionalities facilitates cyclisation of the cyano groups by the amine, hydroxyl and epoxy functions. During cure reaction, the epoxy groups underwent ring-opening in presence of amino NPN leading to oxazolidones, phthalocyanins, triazine and so on, in the cured network along with the built-in GO moieties (Scheme 5.12). Time-resolved IR spectra of APN/GO-5 at 250 °C for varying cure duration are shown in Figure 5.17. With the increase in curing time, it is found that the characteristic nitrile absorption at $2,230\,\mathrm{cm}^{-1}$ in APN decreased with a concomitant reduction in the epoxy group

(916 cm^{-1}) absorption. After 5 h at 250 °C, the absorption due to the nitrile peak completely disappeared. This clearly indicated the incorporation of GO into the cured network.
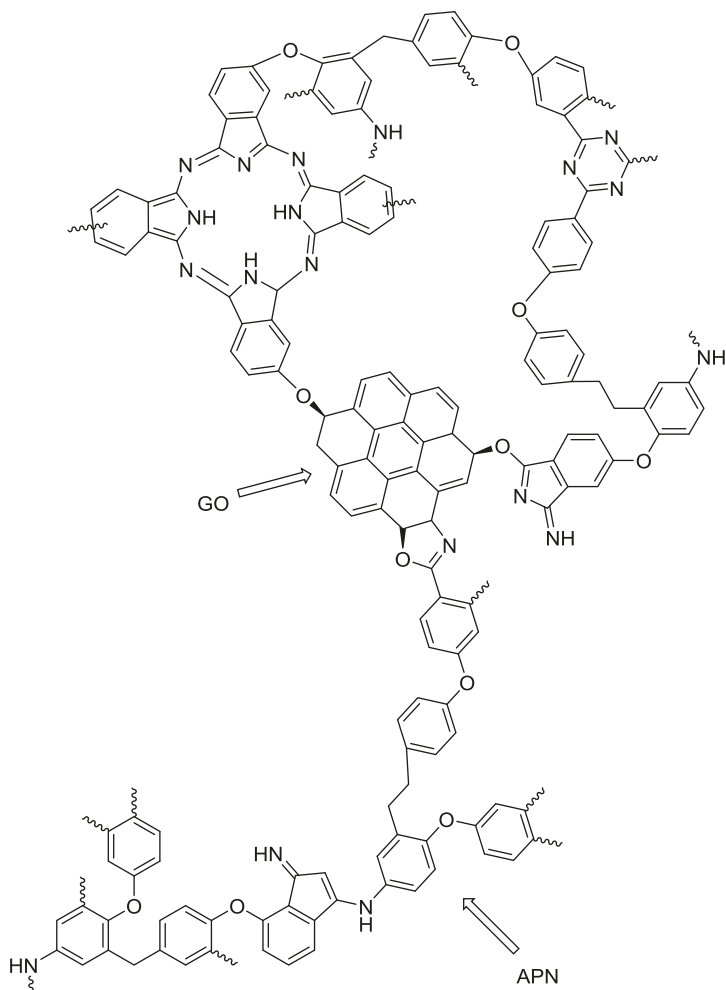
Scheme 5.12: GO-induced PN cured network.

The TGA results show that the thermal stability of the cured blends lowered in the presence of GO. Pure GO exhibited a decomposition temperature at around 160 °C, whereas for APN it was around 420 °C. The char yield for APN at 900 °C is around 78% against that for GO around 52%. Thus, about 25% decrement was observed for the blend composition containing higher proportion of GO. The decrease in thermal stability with higher loadings of GO may be attributed to the loss of easily
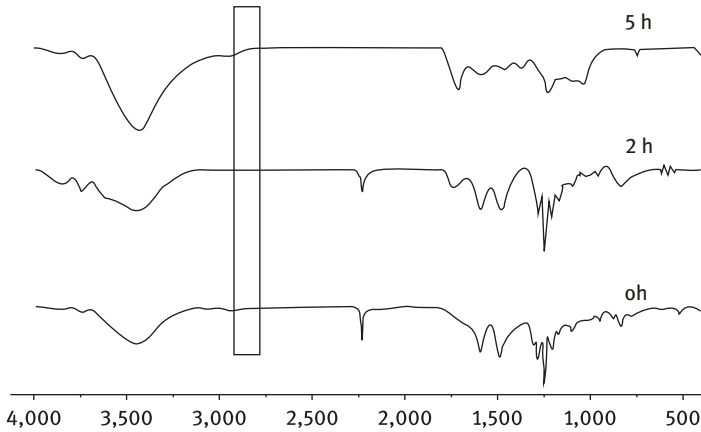
Figure 5.17: Time-resolved FTIR spectra of APN/GO blend at 250 °C.

decomposable oxygen-containing moieties on the GO. SEM images of freshly fractured surfaces of APN/GO blends show plate-like morphology with reasonably good dispersion of GO throughout the matrix as observed from Figure 5.18(a). GO has a flaky texture and for APN blends with high GO loading, a layered microstructure was exhibited as shown in Figure 5.18(b). The composites with higher GO content exhibit a ductile-like fracture pattern showing more plastic deformation characteristics. This is advantageous for the processing of APN-based composites that are generally difficult to process owing to their brittleness.

In another report, a method for the in situ synthesis of multi-walled carbon nanotube (MWCNT) in a bulk solid composition from the pyrolysis of a mixture formulated from $Co_2(CO)_8$ and various high-temperature PN resins was reported [69]. Initially, $Co_2(CO)_8$ was decomposed to cobalt which, in turn, reacted with the developing fused aromatic rings of PN resins, followed by carbonisation process above 500 °C to form a reactive carbon–cobalt nanocomposition that acted as a carbon nanotube (CNT) precursor. On further heating to 800 °C, carbon–cobalt nanocomposition was converted to MWCNT and cobalt nanoparticles. MWCNT were more than 100 mm long with tube diameter around 25–50 nm.

Recently, polymer inorganic nanocomposites have gained a lot of attention since a great number of benefits can be obtained in terms of thermal, mechanical, rheological, electrical, catalytic, fire retardancy and corrosion resistance properties. Derradji et al have studied on the impact of series of micro-sized silicon carbide particles, SiN and titania nanoparticles on BPhA-based PN resin. These inorganic particles are used as reinforcements after treatment with silane coupling agents such as KH-550 and GX-540 [70–72]. This allows a good dispersion and adhesion between particles and resin and thereby improve the thermomechanical properties of composites. The presence of these ceramic particles does not catalyse the cross-linking of PN
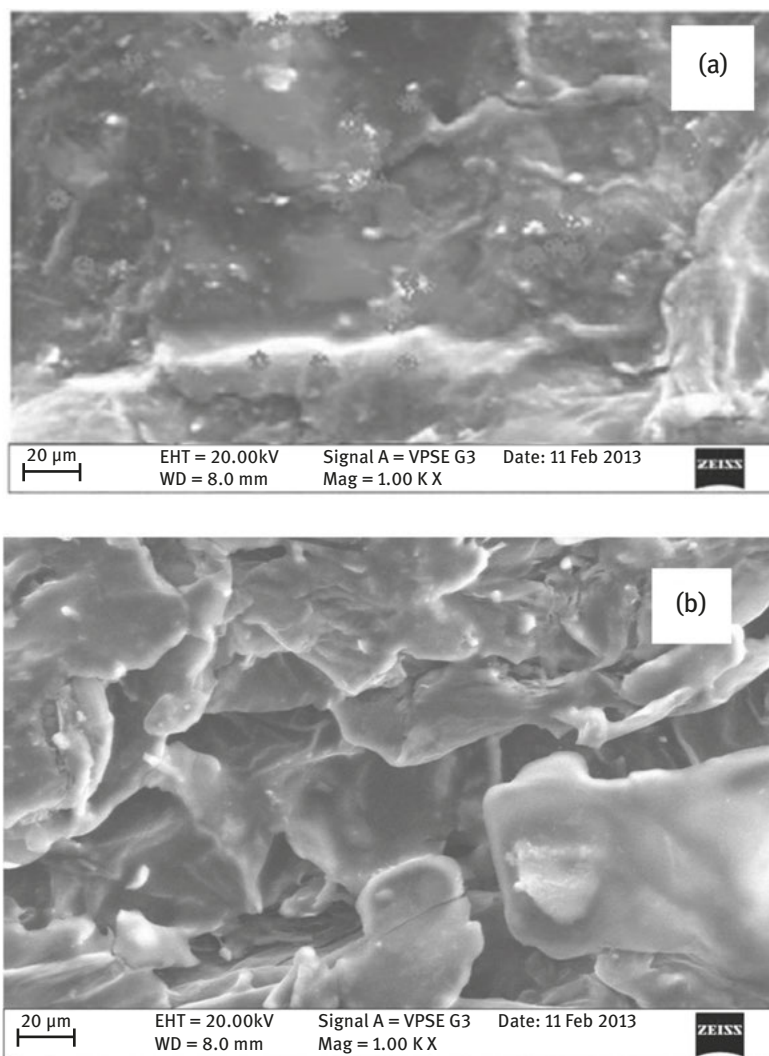
Figure 5.18: SEM images of cured (a) APN/GO-1 and (b) APN/GO-4 blends. Reproduced with permission from T.M. Robert, D. Augustine, D. Mathew and C.P.R. Nair, *RSC Advances*, 2015, 5, 1198. ©2015, Royal Society of Chemistry [67].

polymers but increases the viscosity of matrix and results in increase in curing temperatures. Microhardness value of BPhAPN was enhanced from 380 MPa to 536 MPa for 20 wt% SiC loading and 501 MPa at 6% nanotitania loading, flexural strength and modulus of the composites increased by 75.7 MPa and 1.7 GPa at 20 wt% SiC loading. Micro and nano inorganic particles act as thermal insulators and enhances the thermal stability of composites. For neat resin cured with 4-APPN, $T_{5\%}$ and $T_{10\%}$ (10%

mass loss temperature) were 459.8 °C and 488.7 °C, respectively, with Y_c (800 °C) of 69.7%. At 20% SiC loading ($T_{5\%}$ − 497.8 °C; $T_{10\%}$ − 548.2 °C; Y_c (800 °C) − 83.5%), for 15% SiN loading ($T_{5\%}$ − 496.8 °C; $T_{10\%}$ − 547.2 °C; Y_c (800 °C) − 83.5%) and at 6% titania loading ($T_{5\%}$ − 480.5 °C; $T_{10\%}$ − 552.5 °C; Y_c (800 °C) − 78.5%). T_g of unfilled resin was 300 °C, which increased by 38 °C for 20% SiC and increased by 60 °C for 15% SiN and 6% titania loading. Another recent attempt in the domain of nanocomposites of PNs is utilising polyhedral oligomeric silsesquioxane (POSS) [73]. Two different POSS cage structures such as epoxycyclohexyl POSS (EP0408) and *N*-phenylaminopropyl POSS (AM0281) were used with BPhPN in the presence of BAPP (4,4′-bis(4-aminophenoxy)biphenyl) as curing agent. These combinations exhibited two steps in their cure process: (1) prepolymerisation and (2) triazine formation. The activation energies for the neat polymers and EP0408- and AM0281-containing polymers were 135, 129 and 78 kJ/mol respectively. Smaller percentage loading of POSS was conducive for higher thermal stability as the POSS particles can enter the triazine network and impart more stability, whereas comparatively in higher percentage of POSS, the network of the polymer will be highly branched at the branching point of the POSS ring, the steric hindrance make triazine difficult to form and the cross-linked density is decreased causing a decreased thermal stability. Because of the similar conditions prevailing, the T_g of the polymers also followed a similar trend, that is, at lower concentration of POSS, the stable network formed can effectively hinder the segmental motion of the chain leading to higher T_g. Modification of PN materials using thermally conductive inorganic particles is an effective way to develop thermally conductive PN composites [74]. Hexagonal BN is a good choice due to its high thermal conductivity, low dielectric constant along with a good thermal stability and an excellent resistance to oxidation and chemical corrosion. The thermal conductivity value was 4.69 W/m K at 30 wt% loading of BN. The mechanical property of the composite also got altered as the flexural strength and modulus of the nanocomposites reinforced with the treated nano-BN increased by 115 MPa and 6.6 GPa, respectively, when moving from 0 to 30 wt.% attributable to the ameliorated state of dispersion achieved with the silane coupling agent. $T_{5\%}$ reached at 551 °C with char yield of 92.2% (800 °C). This is the highest value ever reported in the field of PN-based micro- and nanocomposites. The utilisation of MAX phase ceramic particles such as Ti_3SiC_2 nanofillers imparted about 233% gain (from 0.18 W/m.K to 0.6 W/m.K) in the thermal conductivity compared to neat PN resin [75]. Max phases are ductile ceramics and their addition affected the stress and strain in a different way than the traditional ceramics. The tensile stress value increased to 84 MPa at 15 vol% nano-MAX while strain at break values was about 1.6% which is close to that of neat resin. Addition of these soft ceramic particles to brittle PN matrix do not affect the polymer ductility. This is not the case with conventional ceramics such as Al_2O_3 and TiO_2. In addition, toughness of neat resin was significantly enhanced by 79, 91 and 123% with 5, 10 and 15 vol% of MAX phases. Slight improvement in toughness about 19 and 16% can only be achieved with SiC and ZnO loading.

5.5 Potential high-end applications of phthalonitrile polymers and their composites

Modern design concepts in aerospace, space vehicles and re-usable shuttles have pushed the temperature requirements for polymeric materials into even higher positions. Therefore, the improvement or modification of resin systems to introduce further functions such as wear resistance, lower shrinkages, better impact resistances, higher surface protection, flame retardancy and so on, are required. PN polymers are considered as potential candidate matrices for high-temperature performing composites widely used for the technologically advanced areas of aerospace and aircrafts. These application areas are dominated by special polymers such as PBI, PT resins, PMR systems and so on. However, these systems with T_g, of the order of >300 °C were short lived and have drawbacks such as processability.

Though not as widely used as PI, variants of PN resins in composites are gaining attraction because they offer a wide range of tailorable matrices to meet thermal challenges. Heterocyclic rigid networks impart PN systems a higher service temperature (>371 °C) than other high-temperature thermosetting resins.

As described previously, the fire performances of PN-based carbon and glass composites are superior to that of any other thermoset-based composite currently in use for aerospace, ship and submarine applications. They are considered as an excellent substitute for PBI and PMR resins for high-temperature environments. To list a few possible avenues where these high-performing systems are being actively considered for system level application include the following:

– Low cost replacement for metallic structures. Composite design technologies have been developed and successful in lowering manufacturing costs that recommend them over metal designs.
– As upper stage structural components such as payload structures, satellite frame works, solar panel wings, antennas, optical structures, thermal shields, motor cases and nozzles, propellant tanks, pressure vessels and so on.
– High-temperature performing adhesives (>400 °C) for related applications in re-usable launch vehicles and so on.
– As matrices for ablative composites in solid rocket motor nozzles. PN, being high-temperature resistant addition curable resin systems offer the advantage as the composite nozzle components be fabricated without voids unlike the conventional phenolic resin-based condensation polymerisation systems. This facilitates processing of composites at reduced cure pressure and eliminates the need of degassing the composite during the processing.

In this chapter, an attempt has been made to take a review of the PN blends and composites from their initial to contemporary status emphasising the tailor-ability of the system. The properties of PN can be tailored by preparing blends with high-

performing thermosets or thermoplastics, copolymerisation or by means of nano-material incorporation. The commercially important polymers such as epoxy resins, phenolics, BMI, PEN or PEEK have been blended or such moieties have been anchored in the backbone of PN oligomers. In most of the cases, an improvement in the resultant composition was achieved either in terms of improved thermal or mechanical properties or improvement in toughness of the inherently brittle PN polymers. Nanomaterials such as GO and CNT are incorporated into the PN matrix to alter the cure profile and final properties of the systems. The available reports show that the fire performance of PN-based carbon and glass composites are superior to that of any other thermoset-based composite currently in use for aerospace, ship and submarine applications. Thus, PN are poised to emerge as an excellent substitute for PBI and PMR resins for high-temperature environments.

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