Polymerization of *N*-phenylnadimide: a model for the crosslinking of PMR-15 polyimide

J. N. Hay, J. D. Boyle and S. F. Parker
BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, UK

and D. Wilson
BP Advanced Materials Inc., The E. F. Hutton Building, Suite 200, 27401 Los Altos, Mission Viejo, CA 92691, USA

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Compression moulding of *N*-phenylnadimide has been used as a model for the high-temperature crosslinking of PMR-15 polyimide. Nuclear magnetic resonance and Fourier-transform infra-red spectroscopies were used to characterize the polymer structure. The results indicated the occurrence of competing mechanisms depending on the cure temperature. At higher cure temperatures ring opening of the norbornane bridge took place to give a polymer of increased crosslink density. The postulated crosslinking mechanisms can help to rationalize the observed properties of PMR-15, particularly microcracking susceptibility.

(Keywords: PMR-15; *N*-phenylnadimide; crosslinking; mechanism; microcracking; spectroscopy)

INTRODUCTION

General

In less than 20 years advanced composites have become established as efficient high-performance materials and their use is expanding rapidly. The term 'advanced composite' was coined to describe a material consisting of a high-performance fibre such as boron, carbon or aramid in a matrix that is usually polymeric. The major driving force for the use of composites is reduced weight brought about by high stiffness/weight and high strength/weight ratios.

Up to now composites based on epoxy resin matrices have dominated the technology. However, their application is limited to maximum use temperatures of about 130°C. There are many applications that require use temperatures substantially in excess of this; aero-engines and military aircraft are prime examples.

Such a requirement has stimulated an interest in high-temperature polymers. However, successful research in this area has been severely hampered by the necessity to achieve thermal stability along with processability.

PMR-15 polyimide

At present the front runner in the race to develop a high-temperature resin is the NASA-developed polyimide 'PMR-15'. PMR stands for 'polymerization of monomeric reactants' and refers to the way in which carbon fibres are impregnated with a solution of the monomers which are then polymerized *in situ*. This material is essentially based on a norbornene end-capped benzophenonetetracarboxylic acid dianhydride (BTDA)/methylene dianiline (MDA) oligomer. See *Figure 1* for the chemistry.

The key point to note is the crosslinking reaction, the conventional view of which employs reverse Diels–Alder (RDA) chemistry. It is this crosslink that provides the basis for the exceptional thermal stability of PMR-15. The use temperature of PMR-15 is in the 280–300°C range. At present no other commercial system offers the balance of properties and processability.

Despite being the leading system available today PMR-15, like all materials, has a number of limitations affecting its widespread use. Included in these is its susceptibility to microcracking from thermal cycling. Such cracking results in a loss of mechanical properties and a reduction in oxidative resistance.

Earlier work by BP and Rolls-Royce[1] showed that it is possible to cure PMR-15 at low temperature to produce a material with a high resistance to microcracking. This improved resistance was ascribed to a reduction in thermal stress brought about by the actual reduction in cure temperature and perhaps by the formation of a polymer network of reduced resin modulus. The latter point proved difficult to substantiate because of the problems encountered in the fabrication of reliable neat resin plaques. These difficulties led to subsequent work being directed towards the use of model compounds, particularly *N*-phenylnadimide, as a route to throwing light on possible differences in polymer structure brought about by the different curing temperatures.

This paper reports on the polymerization of *N*-phenylnadimide at a variety of temperatures with subsequent characterization of the polymer, particularly by n.m.r. and *FT*i.r.

EXPERIMENTAL

Synthesis of materials

endo-*N*-Phenyl-5-norbornene-2,3-dicarboximide (*N*-

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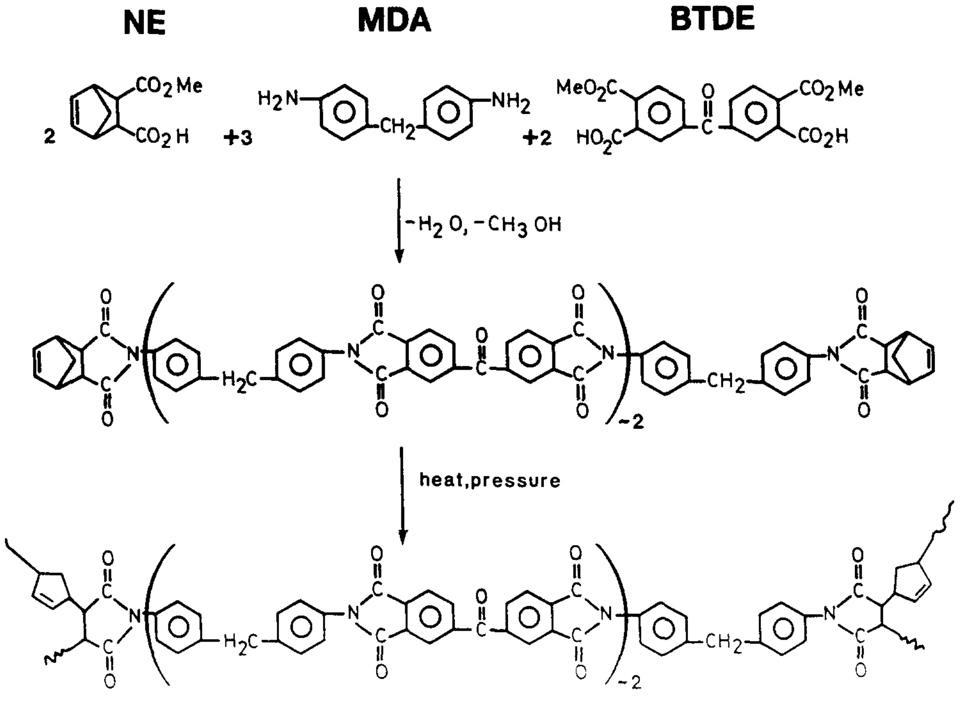

Figure 1 PMR-15 chemistry

phenylnadimide, NPN) was prepared by the method of Delvigs[2].

N-Phenylsuccinimide was prepared by an analogous route to the *N*-phenylnadimide, m.p. 146–148°C (lit. 154–155°C[3]).

Polymerization of N-Phenylnadimide

N-Phenylnadimide was polymerized thermally using a compression-moulding technique. The mould was filled with compacted, powdered *N*-phenylnadimide and all gaps sealed with Kapton film and Kapton adhesive tape. The mould was placed in a hydraulic press and subjected to the following cure cycle:

(1) Apply contact pressure.
(2) Heat to 218°C in 57 min.
(3) Hold at 218°C for 50 min.
(4) Apply 400 psi pressure.
(5) Increase temperature to final cure temperature at 3°C min^{-1}.
(6) Hold at final cure temperature for 12 h.
(7) Allow press to cool naturally to room temperature prior to demoulding.

Final cure temperatures used were 270°C (NPN-270), 300°C (NPN-300) and 330°C (NPN-330).

Characterization of polymers

^1H and ^{13}C n.m.r. ^1H and ^{13}C n.m.r. spectra of *N*-phenylnadimide and its polymers were recorded as solutions in chloroform-d on a Jeol JNM GX400 n.m.r. spectrometer at 399.65 MHz for ^1H and 100.4 MHz for ^{13}C. In each case spectrometer conditions were chosen to ensure that good quantitative data were obtained.

^{13}C d.e.p.t. spectra[4] were also recorded to assist the assignment of the spectra. This technique yields spectra in which CH and CH_3 carbons are in phase, CH_2 carbons are inverted and quaternary carbons are suppressed.

FTi.r. Infra-red spectra of *N*-phenylnadimide and its polymers were obtained on a Nicolet 7199B Fourier-transform infra-red (*FT*i.r.) spectrometer as thin films on a KBr plate. Some 2000 scans at 1 cm^{-1} resolution were co-added to give the final spectrum. The thin films were prepared by evaporating the solvent from a dichloromethane solution of the imide on a KBr plate.

RESULTS

Interpretation of the n.m.r. spectra

Figure 2a shows the normal ^{13}C spectrum of *N*-phenylnadimide polymer produced at 270°C. The corresponding d.e.p.t. spectrum with CH_2 carbons inverted, CH carbons in phase and quaternary carbons suppressed is shown in *Figure 2b*. An expansion of the region containing the aliphatic carbons for this material is shown in *Figure 3a* and the equivalent region of the polymer prepared at 330°C is shown in *Figure 3c*, with the corresponding d.e.p.t. spectra being shown in *Figures 3b* and *3d* respectively. Assignments of the resonances in the spectra are given in *Table 1*. The spectrum of NPN-270 consists of a mixture of broad and sharp peaks. The sharp lines are due to low-molecular-weight species such as monomers and dimers whereas the broad lines arise from polymeric materials. Four low-molecular-weight species can be positively identified[5] and are shown in *Figure 4*. The broad lines from the polymeric species have not been assigned but their shifts are consistent with structures proposed in the literature[6]. The ^{13}C n.m.r. spectrum of NPN-330 (*Figures 3c* and *3d*) shows very few sharp resonances compared to that of NPN-270 (*Figures 3a* and *3b*), indicating the near-absence of low-molecular-weight material in the polymer obtained at higher temperature. However, one sharp peak is observed at 28 ppm (*Figures 3c* and *3d*). This resonance is not detected in the NPN-270 polymer (*Figure 5a*) but can be seen in the NPN-300 material at a low level (*Figure 5b*). In addition another new resonance which grows in intensity at a similar rate is detected at 176.1 ppm. These resonances were confirmed

Table 1 Assignment of the ^{13}C n.m.r. spectra of polymers of *N*-phenylnadimide

Peak number[a]	Chemical shift, δ (ppm)	Assignment[b,c]
1	177.27 176.79 176.62	Imide C=O
2	139.47	*exo–endo–exo* (a)
3	137.65	*exo* (a)
4	135.44	*endo–exo–exo* (a)
5	134.29	*endo* (a)
6	131.74 131.65	Aromatic carbons of monomer and polymers
7	128.88	
8	128.37	
9	126.14	
10	53.10	*endo–exo–exo* (d)
11	51.90	*endo* (d), *endo–exo–exo* (*b*)
12	50.83	*exo–endo–exo* (b)
13	50.06	*exo–endo–exo* (e)
14	48.99	*endo–exo–exo* (e)
15	47.56	*exo* (b)
16	46.03	*endo–exo–exo* (g)
17	45.44	*exo* (c), *endo* (b), *exo–endo–exo* (g)
18	45.15	*endo* (c)
19	42.68	*exo* (d), *exo–endo–exo* (d)
20	42.21	*exo–endo–exo* (c)
21	41.58	*endo–exo–exo* (c)
22	30.37	*exo–endo–exo* (f)
23	29.86	*endo–exo–exo* (f)
24	28.07	*N*-phenylsuccinimide

[a] See *Figures 2* and *3*
[b] See *Figure 4*
[c] Some of the assignments of smaller peaks are tentative

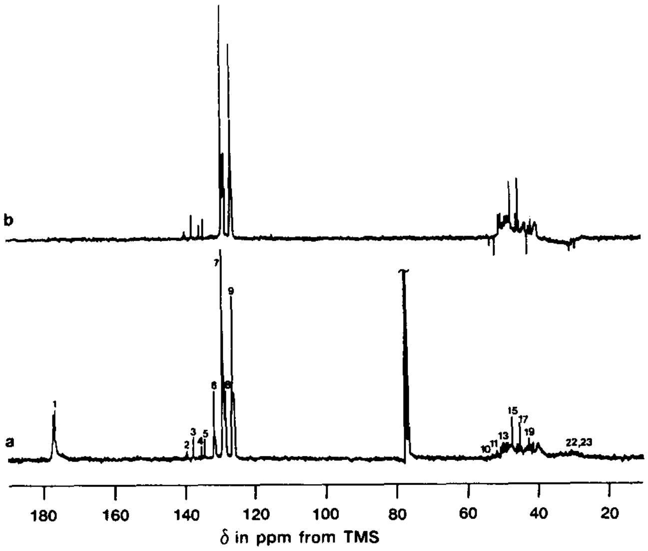

Figure 2 ^{13}C n.m.r. spectra of *N*-phenylnadimide polymerized at 270°C: (a) normal spectrum and (b) d.e.p.t. spectrum

to be due to *N*-phenylsuccinimide by addition of an authentic sample of this species to NPN-330, when the resonances were found to superimpose directly.

A significant increase in the intensity of the resonances in the region 20–35 ppm can be seen in NPN-330 (*Figure 3c*) compared to NPN-270 (*Figure 3a*). Examination of the d.e.p.t. spectrum of NPN-330 (*Figure 3d*) shows that these new resonances are all CH_2 carbons. Ratios of the different types of carbons detected (aromatic, olefinic, aliphatic CH and aliphatic CH_2) measured from the ^{13}C spectra are given in *Table 2*. The ratio of CH:CH_2 carbons decreases with increasing polymerization temperature. No olefinic material is detected in the spectra of NPN-300 or NPN-330.

^1H n.m.r. spectra of the monomer and the three polymers are shown in *Figures 6a–d* and assignments of the numbered peaks are given in *Table 3*. The quantitative ^1H n.m.r. data are given in *Table 4*. There is no olefinic material detected in the ^1H spectrum of either NPN-300 or NPN-330 shown by the absence of resonances between 5 and 6.5 ppm in *Figures 6c* and *6d*. NPN-270 shows some olefinic species (resonances between 5 and 6.5 ppm in *Figure 6b*) although compared with the starting material (*Figure 6a*) only 19% of olefinic material remains. The four major olefinic species in NPN-270 (peaks 4 to 7 in *Figure 6b*) can be assigned to the structures shown in *Figure 4* (*Table 3*) and the molar percentage of each is given in *Table 5*.

Interpretation of the i.r. spectra

The infra-red spectrum of *N*-phenylnadimide is shown in *Figure 7a*. *Table 6* lists the major bands of the *N*-phenylnadimide and their assignments. These are based on work on related molecules, particularly toluene[7], maleimide[8] and norbornane[9]. It can be seen that the

Table 2 Quantification of ^{13}C n.m.r. spectra of monomeric and polymeric *N*-phenylnadimide

	Carbon type[a,b] (%)				
Sample	Aromatic	Olefinic	CH	CH_2	CH:CH_2
NPN	6 (6)	2.1 (2)	3.6 (4)	0.9 (1)	4:1
NPN-270	6	0.6	4.6	2.0	2.3:1
NPN-300	6	0	3.9	1.6	2.4:1
NPN-330	6	0	2.9	1.6	1.6:1

[a] Figures in parentheses are theoretical values
[b] Six aromatic carbons are assumed for the calculation

Table 3 Assignment of ^1H n.m.r. spectra of monomeric and polymeric *N*-phenylnadimide

Peak number[a]	Chemical shift, δ (ppm)	Assignment[b]
1	7.36 7.34	Aromatic H of monomer and polymers
2	7.30 7.28	
3	7.10 7.08	
4	6.26	*exo* (a)
5	6.17	*endo* (a)
6	6.10	*exo–endo–exo* (a)
7	5.96	*endo–exo–exo* (a)
8	3.35 3.26	*endo* (c)
9	3.25 3.24	*endo* (b)
10	2.69	*N*-phenylsuccinimide CH_2
11	1.64	*endo* (d)
12	1.62 1.46 1.43	

[a] See *Figure 6*
[b] Some of the assignments of the smaller peaks are tentative

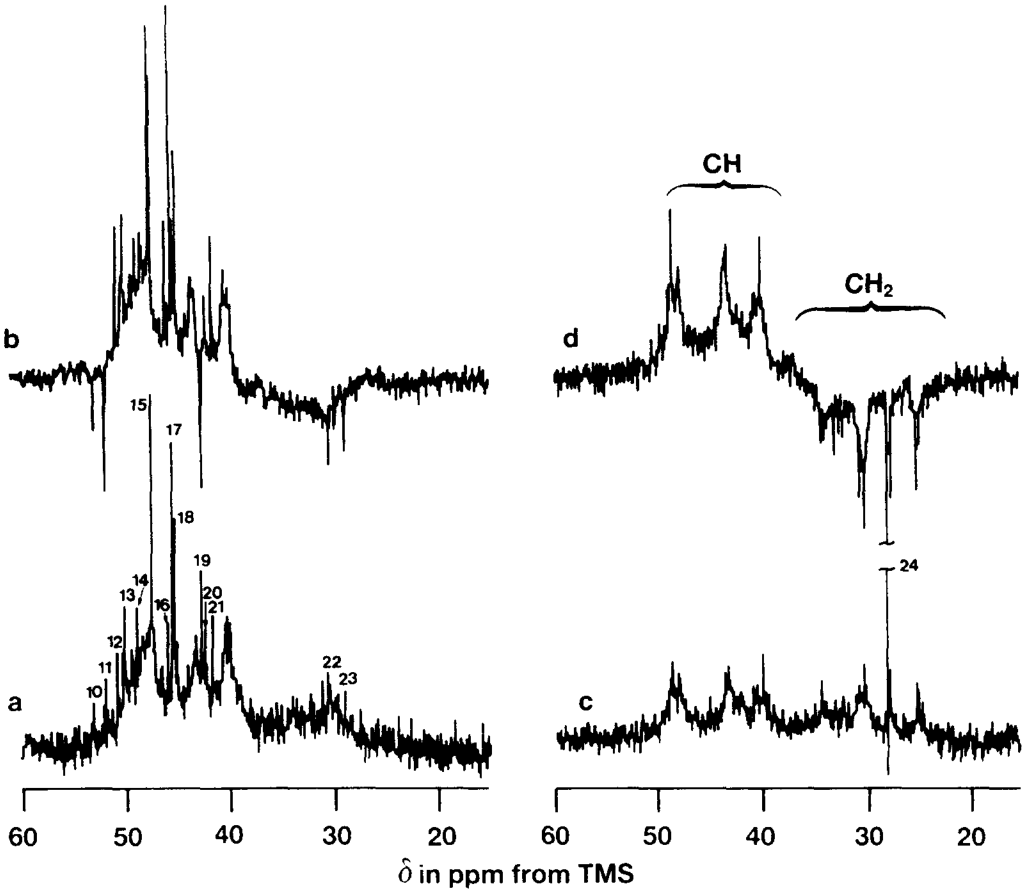

Figure 3 ^{13}C n.m.r. spectra of the aliphatic carbons of *N*-phenylnadimide polymerized at: (a) 270°C, (b) d.e.p.t. spectrum of 270°C polymer; (c) 330°C and (d) d.e.p.t. spectrum of 330°C polymer

Table 4 Quantification of ^1H spectra of monomeric and polymeric *N*-phenylnadimide

Sample	H type[a,b] (%) Aromatic	Olefinic	Aliphatic
NPN	5 (5)	2.0 (2)	6.0 (6)
NPN-270	5	0.4	7.4
NPN-300	5	0	7.5
NPN-330	5	0	7.3

[a] Assuming five aromatic H
[b] Figures in parentheses are the theoretical values

Table 5 Quantification of olefinic H from ^1H spectrum of *N*-phenylnadimide polymerized at 270°C

Olefin type	Molar %
exo	21
endo	19
exo–endo–exo	7
endo–exo–exo	12
Others	41

bands may broadly be divided into three groups: those characteristic of the phenyl ring, those of the imide ring and those of the norbornene end-cap. The similarity of the observed frequencies to those of the model compounds[6–8] strongly suggests that there is minimal coupling of the vibrations of the three functionalities. Thus it is reasonable to use the frequencies as flags for the presence or absence of a particular group. In the context of the present investigation, it is unfortunate that most of the norbornene-derived modes are weak. However, the 3000 cm^{-1} band, although still weak, is relatively strong in comparison to the other C–H stretching frequencies and is definitely related to the presence of the C=C group. A second mode characteristic of the C=C group is the out-of-plane bending motion of the olefinic C–H bonds at 719 cm^{-1}. This is reasonably strong and a good group frequency.

The infra-red spectrum of the polymer prepared at 300°C is shown in *Figure 7b*. The spectra of the polymers prepared at 270°C and 330°C are very similar. *Table 7* lists the observed bands and their assignments for the three polymers. Once again, the bands may be divided into three main classes: those of the phenyl ring, those of the imide ring and those assignable to aliphatic CH_2 and CH groups. The polymer thus appears to be an *N*-phenylnadimide attached to a saturated backbone. The strong resemblance of all three polymer spectra to each other implies that this structure is common to all three materials.

The striking feature of *Figures 7a* and *7b* is the simplicity of the polymer spectrum as compared with that of the monomer. Inspection of the figures and a comparison of *Tables 6* and *7* show that the difference is due to the absence of any features that could reasonably be assigned to the norbornene end-cap. In particular the only bands above 3000 cm^{-1} are assigned to the phenyl ring, and the 719 cm^{-1} band has disappeared in all three

Table 6 Infra-red band positions (cm^{-1}) and assignments for *N*-phenylnadimide

Position[a]	Assignment
3072w	Phenyl C–H stretch
3059w	Modes involving the olefinic C–H stretch
3024w	
3000w	
2979w	Aliphatic CH_2 and CH stretching modes
2954w	
2946w	
2879w	
1767w	Symmetric C=O stretch
1707vs	Asymmetric C=O stretch
1597w	Phenyl ring stretch
1498s	
1454w	
1376s	Imide ring symmetric CNC stretch (imide II)
1336m	
1287m	Imide ring asymmetric CNC stretch (imide III)
1153w	Norbornene mode
1121w	Norbornene CH_2 bend
1057w	Norbornene skeletal modes and C–H bend
962w	
907w	
845m	
742s	Phenyl C–H out-of-plane bend
719s	Olefinic C–H out-of-plane bend
694s	Phenyl ring deformation
620s	Imide C=O bend

[a] vs = very strong, s = strong, m = medium, w = weak

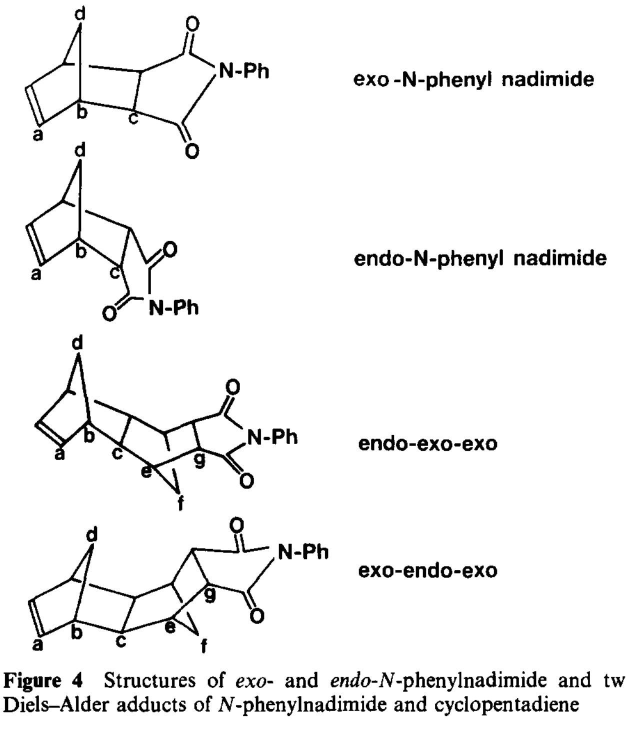

Figure 4 Structures of *exo*- and *endo*-*N*-phenylnadimide and two Diels–Alder adducts of *N*-phenylnadimide and cyclopentadiene

polymers. Additionally, the relative increase in intensity of the bands assigned to the saturated C–H bonds is consistent with the picture of complete polymerization at all three temperatures.

This conslusion is surprising in view of the n.m.r. evidence that showed approximately 20% of residual unsaturation in NPN-270. The failure to detect any evidence of this presumably means that the bands are weak and/or overlapped.

N.m.r. has also shown that NPN-330 contained significant quantities of *N*-phenylsuccinimide. Attempts to find evidence of this by deconvolution of the carbonyl band were unsuccessful. In view of the fact that the carbonyl bands of *N*-phenylsuccinimide and the polymer are only separated by $4\,cm^{-1}$ with halfwidths of approximately $20\,cm^{-1}$, the failure to resolve the carbonyl band is not surprising.

DISCUSSION

Reverse Diels–Alder resins

Background. Reverse Diels–Alder (RDA) resins are so named because of the postulated mechanisms involved in

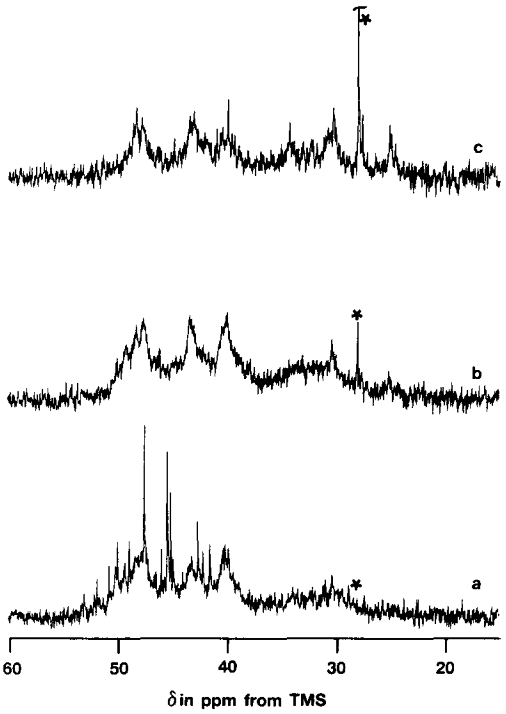

Figure 5 ^{13}C n.m.r. spectra of the aliphatic carbons of *N*-phenylnadimide polymerized at: (a) 270°C, (b) 300°C and (c) 330°C indicating the formation of *N*-phenylsuccinimide

Table 7 Infra-red band positions (cm^{-1}) and assignments for the poly(*N*-phenylnadimides)

Position[a]			
270°C	300°C	330°C	Assignment
3065w	3066w	3065w	Phenyl C–H stretch
3047w	3046w	3047w	
2959m	2954m	2955m,br	Aliphatic methylene and methine C–H stretch
2890sh	2892sh	2885sh	
1773w	1772w	1765w	Symmetric C=O stretch
1709vs	1711vs	1714vs	Asymmetric C=O stretch
1598w	1598w	1598w	
1499s	1500s	1500s	Phenyl C–C stretch
1456vw	1456w	1456w	CH_2 scissors
1376s	1377s	1381s	Imide II
1289vw	1289vw	1289vw	
		1269vw	
1182s	1180s	1183s	Imide III
751m	753m	757m	Phenyl C–H out-of-plane bend
737sh	738sh	737sh	
691m	691m	693m	Phenyl ring deformation
615w	617w	621w	

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, sh = shoulder

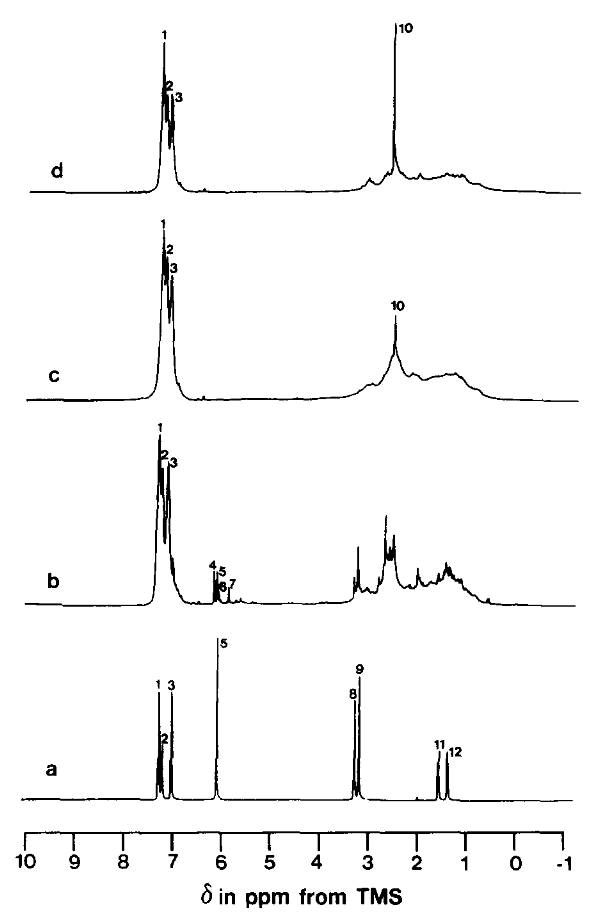

Figure 6 ^{1}H n.m.r. spectra of (a) *N*-phenylnadimide and its polymers obtained at (b) 270°C, (c) 300°C and (d) 330°C

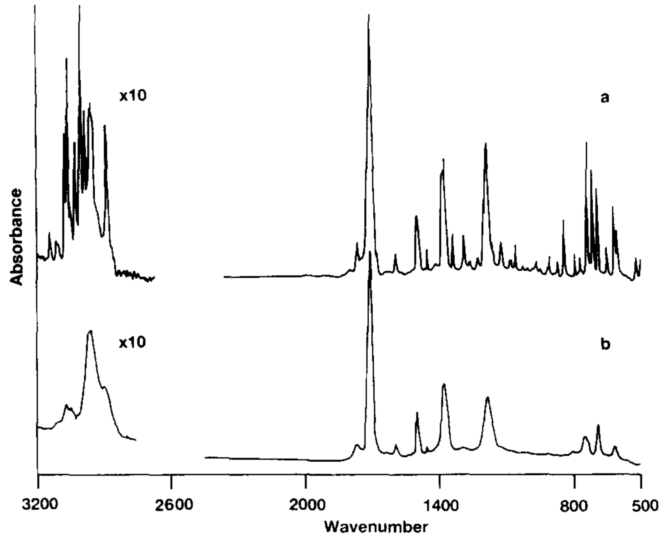

Figure 7 *FT*i.r. spectrum of (a) *N*-phenylnadimide and (b) *N*-phenylnadimide polymerized at 300°C

their curing (*Figure 8*). This is discussed in detail later. These materials are polyimides with norbornene end-groups, which can be further polymerized (at elevated temperatures) to give a thermosetting resin.

Evidence for the RDA reaction. The original evidence for the occurrence of the retro Diels–Alder reaction during cure was inferred from the observation of a dicyclopentadiene odour. A number of studies have provided a more scientific basis for this conclusion.

Studies of the thermal polymerization of bisnadimides have demonstrated the evolution of cyclopentadiene by RDA reaction, but only in quantities well below the theoretical value[10]. These compounds also exhibit a strong d.t.a. exotherm corresponding to the RDA reaction. A more recent study using a combined t.g.a.–g.c.–m.s. technique has shown that the cyclopentadiene is evolved in two distinct temperature regions, corresponding to the RDA reaction of the *endo* and *exo* isomers[11].

Work at BP has concentrated on studies of PMR-15 itself[1]. Several analytical techniques have been used to demonstrate the occurrence of the RDA reaction in a qualitative way. Pyrolysis g.c. shows cyclopentadiene evolution taking place above 240°C, while Raman spectroscopy shows the appearance of a band due to the maleimide double bond during the cure cycle. A combined t.g.a.–d.t.a.–m.s. study of PMR-15 showed two distinct regions of cyclopentadiene evolution. The smaller of the two, centred at 200°C, can be attributed to the RDA of the *endo* isomer, whilst the larger evolution, centred at 260°C, probably arises from the *exo* isomer.

The above observations demonstrate the occurrence of the RDA reaction as an important reaction of the nadimide end-group at elevated temperatures, but the extent to which it occurs during moulding under pressure has not been established.

Evidence for RDA 'driven' crosslinking reactions. It is important that all the cyclopentadiene evolved by RDA reaction is recaptured via crosslinking so that voids are not produced in the composite. Kinetic experiments conducted by NASA provide strong evidence that this is indeed the case[12]. The crosslinking reaction was found to follow first-order kinetics with pre-exponential factor and activation energy in agreement with the values expected for a unimolecular thermal fission reaction. The rate-determining step of the process is therefore the RDA reaction, which is followed rapidly by crosslinking. Crosslinking of PMR-15 is therefore a direct consequence of the occurrence of the RDA reaction.

Conventional crosslinking mechanism. The conventional view of the PMR-15 crosslinking reaction is that originally proposed by NASA (*Figure 8*). RDA reaction of the norbornene end-groups leads to maleimide groups and cyclopentadiene, which then undergo a thermally induced free-radical polymerization reaction to a crosslinked polymer containing cyclopentene crosslinks. *FT*i.r. studies conducted at BP have tended to support this mechanism by showing, in laminates, the presence of

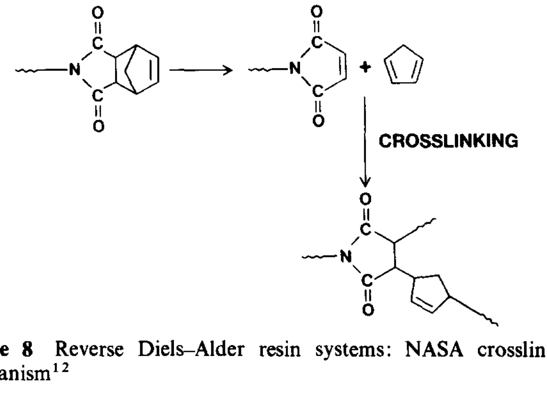

Figure 8 Reverse Diels–Alder resin systems: NASA crosslinking mechanism[12]

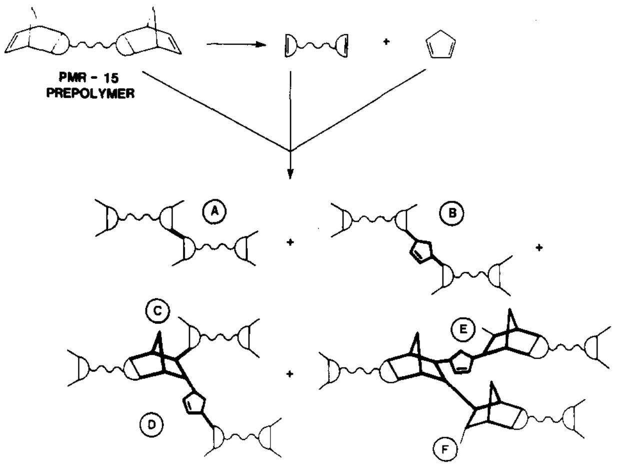

Figure 9 Possible crosslinking mechanisms of PMR-15 based on earlier BP/Rolls-Royce studies[1]

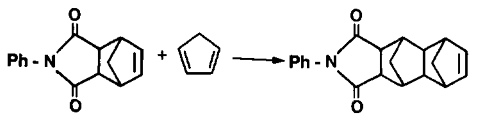

Figure 10 Formation of doubly bridged adducts (after ref. 5)

an absorption at 743 cm^{-1} attributable to the cyclopentene crosslink[13].

PMR-15 properties

The properties, both mechanical and thermal, of a thermoset such as PMR-15 are a consequence of several structural features of the resin. High stiffness and thermal stability are imparted by the presence of rigid aromatic and polyimide heterocyclic units. The nature of the crosslink reaction, the crosslink type and density also play a significant role in determining resin modulus and thermo-oxidative stability.

Microcracking due to thermal cycling formed the basis of an earlier study by BP and Rolls-Royce on the effect of cure temperature on PMR-15 properties[1]. This study concluded that microcracking could be reduced substantially by reducing the final cure temperature of PMR-15 (see 'Introduction'). The results could be rationalized in part by the presence of a different type of crosslink structure at 270°C compared with 330°C. The physical properties of the composites were consistent with a higher proportion of longer crosslinks being formed between the imide rings at lower temperatures. These conclusions can be rationalized by a scheme such as that shown in *Figure 9*.

The crosslinking mechanism operative is governed by the rate of the RDA reaction. At low temperatures, this rate is low and cyclopentadiene is generated in the presence of significant concentrations of norbornene groups. This would favour the formation of crosslinks of type D and E. Conversely, at high temperature, a rapid evolution of cyclopentadiene would favour crosslinks of type B.

Unfortunately, the difficulties in characterizing these highly crosslinked, insoluble materials means that absolute confirmation of these postulated structures is impossible. In order to learn more about the crosslinking mechanisms operative, it is necessary to turn to the study of model compounds. The dangers inherent in translating the results of model compound studies to the understanding of 'real' systems need also to be borne in mind.

Model compound studies

Literature studies. Model compound studies reported in the literature have generally used *N*-phenylnadimide as a model for the PMR-15 curing reaction[5,14–16]. Polymerization of *N*-phenylnadimide leads to soluble polymers which are more easily studied by standard analytical techniques. Studies have also been carried out on the cured products from simplified PMR systems such as the 2NE/MDA adduct[6,17]. In these studies, polymerization was initiated either chemically or thermally, usually in a sealed glass tube. The results obtained were mostly in direct contradiction to the conventional view of PMR crosslinking. With one exception[15] it was found that the cyclopentadiene evolved by the RDA reaction did not copolymerize but underwent a further Diels–Alder reaction with the *N*-phenylnadimide double bond to give the doubly bridged adduct (*Figure 10*).

The principal products were found to be the *endo–exo–exo* and the *exo–endo–exo* isomers, consistent with the Diels–Alder reaction with the thermodynamically more stable *exo-N*-phenylnadimide. The kinetic *endo–exo–exo* product is formed at lower temperatures. With the exception of the Chinese study[15], products obtained by the polymerization of the *N*-phenylnadimide showed the complete absence of any unsaturation which could be attributed to the cyclopentene crosslink. Instead, polymerization appeared to take place through the double bonds of the *N*-phenylmaleimide, *N*-phenylnadimide and the double Diels–Alder adduct (*Figure 11*). It was also found that the *exo* isomer polymerizes more readily than the *endo* isomer. This provides further evidence that the cure mechanism differs from the conventionally held view, since RDA reaction of the less thermodynamically stable *endo* isomer should be much faster than that of the *exo*. The rate-determining step for the polymerization in this case is obviously not the RDA reaction but the double-bond polymerization reaction. The solid-state n.m.r. studies of simplified PMR molecules gave results which were in broad agreement with those outlined above[17].

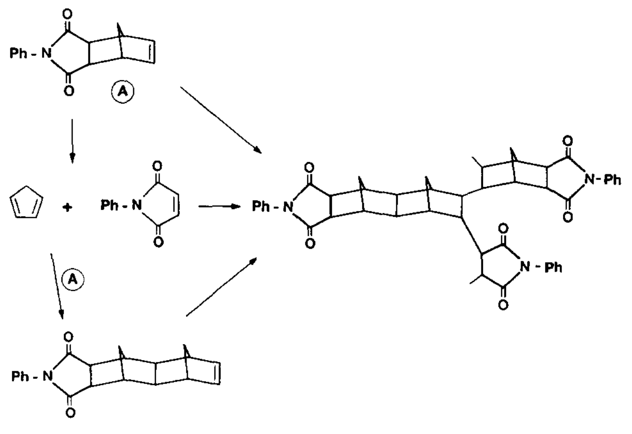

Figure 11 Model compound studies: polymerization scheme (cf. ref. 5)

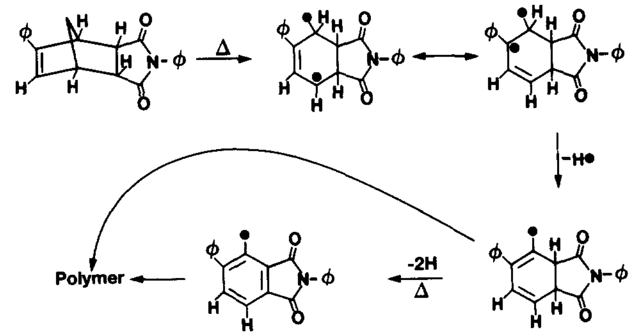

Figure 12 Polymerization of phenyl-substituted *N*-phenylnadimide (after ref. 16)

A further interesting observation was made in a study of the thermal isomerization and polymerization of substituted *N*-phenylnadimide[16]. When the *N*-phenylnadimide had a phenyl substituent on the double bond, a significant quantity of the hydrogenated starting material was formed during thermal cure. This was rationalized by a mechanism involving opening of the norbornene bridge followed by oxidation leading to increasing unsaturation (*Figure 12*). Unreacted starting material then acts as a hydrogen acceptor. The production of radicals by this process was postulated as a contributory factor in the enhanced rate of polymerization observed for the substituted nadimides. No evidence was provided for the presence of increased unsaturation.

BP work on compression moulding of N-phenylnadimide. Original BP/Rolls-Royce work on the effect of cure temperature seemed to lend support to the conventional crosslinking mechanism[1]. This was based on the appearance of a band at 743 cm^{-1} in the diffuse reflectance *FT*i.r. spectra of the laminates, the position of which corresponds to that found in cyclopentene-containing polymers[13]. Model compound studies were carried out to attempt to resolve the discrepancy between this work and the studies described above.

In this recent work, *N*-phenylnadimide was again used as the model, but this time the polymerization was carried out by compression moulding using the same cure cycle as that used to prepare the composite laminates. Final cure temperatures used were 270, 300 and 330°C. As expected, soluble polymers were obtained. The techniques used to study these products were ^{1}H and ^{13}C n.m.r. and *FT*i.r. (see earlier sections).

Surprisingly, these polymers again showed no evidence of simple double-bond unsaturation. Further work is clearly required to identify the functionality producing the 743 cm^{-1} absorption band in the *FT*i.r. spectra of laminates. *N*-Phenylnadimide cured at 270°C had not fully polymerized and contained about 20% monomeric compounds. Identification of these compounds provided further evidence for the *endo–exo* isomerization of the *N*-phenylnadimide, as well as showing the presence of the *endo–exo–exo* and *exo–endo–exo* doubly bridged species.

Detailed analysis of the n.m.r. spectra revealed a number of interesting features:

(a) There was an approximate two-fold increase in the number of methylene groups on polymerizing the nadimide.

(b) The number of aromatic carbons increased relative to the aliphatic carbons with increasing cure temperature.

(c) Increasing cure temperature resulted in a significant increase in the proportion of a product identified as *N*-phenylsuccinimide.

None of these observations can be accounted for by either of the mechanisms discussed above. A partial rationalization of these facts can be postulated based on the mechanism previously proposed only for phenyl-substituted *N*-phenylnadimides[16].

The proposed BP scheme (*Figure 13*) involves the following steps:

(1) Initial double-bond polymerization as postulated previously (*Figure 11*).

(2) Thermal fission of the norbornane bridge in the first-formed polymer.

(3) Oxidation of the resultant ring with concomitant reduction of the *N*-phenylmaleimide double bond.

(4) Double-bond isomerization and further crosslinking (or other reaction) then leads to the product.

The double bond of the resulting maleimide ring would be expected to give a ^{13}C resonance in the same region of the spectrum as the aromatic carbons. There would therefore be an increase in the relative number of aromatic (plus olefinic) carbons and the number of methylene groups. These two features should occur simultaneously with increase in cure temperature. The fact that the relative increase in the number of methylene groups does not follow the precise trend expected may be due to inaccuracies in the integration of the aliphatic region of the ^{13}C spectrum, which is very complex. The *N*-phenylsuccinimide arises from the reduction of the *N*-phenylmaleimide formed by the RDA reaction.

Significance of crosslinking mechanism to PMR-15 properties

The proposed mechanism can account for the increased microcracking tendency observed for high-temperature-cured resin systems.

(1) Microcracking is related to thermal stresses which occur mainly because of the difference in thermal expansion coefficients of the fibre and the resin.

(2) Thermal expansion can be reduced by a number of factors, including a reduction in resin modulus.

(3) In the proposed mechanism, the methylene radical produced by thermal ring opening of the norbornane bridge offers the potential for increased crosslinking in the higher-cure-temperature systems. This would give a tighter or more densely crosslinked structure, which would lead to a resin system of high modulus.

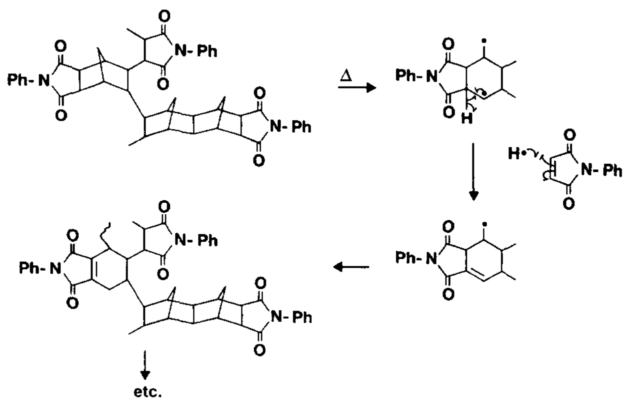

Figure 13 Model compound studies: possible high-temperature polymerization mechanism

(4) Conversely, the less dense crosslinks produced at lower cure temperatures would lead to a reduced resin modulus, reduced thermal stresses and a reduced tendency to microcrack during thermal cycling.

The mechanistic scheme is therefore consistent with the results of the earlier BP/Rolls-Royce study[1].

There is little reason to expect the thermal stability of the postulated structures to differ greatly from resins containing cyclopentene crosslinks. Reaction at the maleimide double bond may be hindered by the tetra-substitution. Alternatively, further reaction of this double bond could lead to crosslinking in the product.

CONCLUSIONS

The thermosetting polyimide, PMR-15, is the leading matrix resin for use in polymer composites capable of continuous use at temperatures around 300°C. It nonetheless suffers from a number of disadvantages, including microcracking due to thermal cycling.

Original work showed that low-temperature curing of PMR-15 gave laminates with a high resistance to microcracking.

This observation was rationalized in terms of the actual cure temperature reduction and possible formation of a polymer network of reduced modulus.

The original hypothesis has been partially confirmed by new model compound studies using *N*-phenylnadimide.

These studies indicate that high cure temperatures lead to structures of high crosslink density, high modulus and therefore greater susceptibility to microcracking.

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