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Hybrid nitrile-based reactive diluent for phthalonitrile resins

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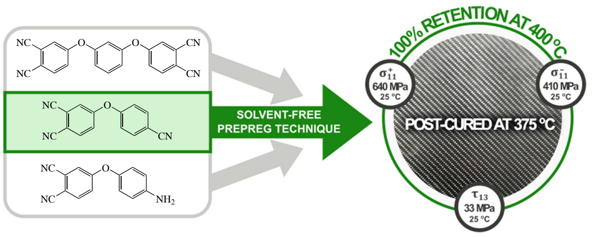
A hybrid diluent containing both phthalonitrile and benzonitrile functions was tested for improvement of phthalonitrile resin processability. The composites were obtained by the solvent-free prepreg technique and characterized by thermal and mechanical tests (σ^{+}_{11} = 640 MPa at room temperature with 100% retention at 400 °C) and preserved 50% of the strength after 1000 h aging at 350 °C.



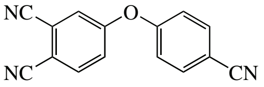
Keywords: phthalonitrile, diaryl ethers, reactive diluent, thermal properties, mechanical properties, polymer composite.

Carbon fiber reinforced polymer composites became essential materials where a combination of light weight and high mechanical strength gives benefits in operation in the industries, such as aerospace industries, sports, electric vehicle production, and alternative energetics. The most commonly used polyether and epoxy resins can be operated only below 120 °C,[1] while thermally stable commercial resins of bis-maleimide[2,3] and cyanate ester[4,5] families can be operated up to 250 °C. Phthalonitrile thermosets demonstrate decomposition temperatures over 500 °C in TGA experiments[6,7] but at the same time lose their mechanical characteristics during long-term operation under oxidative atmosphere above 300 °C.[8,9] Despite that, phthalonitrile matrix composites remain being the most thermally stable materials[10,11] and would demonstrate a unique level of mechanical properties at elevated temperatures,[12,13] exceptional fire retardancy,[14–17] and dielectric properties.[18,19]

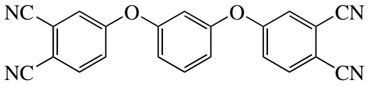
The main disadvantage of phthalonitrile resins is poor processability caused by high melting points of the monomers.[6,20] Several strategies were implicated to improve processability of the resins,[21–26] but only few of them based on the addition of reactive diluents provided the processability matching the requirements of cost-effective composite fabrication techniques such as vacuum infusion, resin transfer molding (RTM), and solvent-free prepregs.[13,16,22,27] Blending different reactive phthalonitriles can be used not only for improving processability of the resins but also for modification of physical and mechanical properties of the composites.[28,29]

The discovery of thermal copolymerization between phthalonitriles and benzonitriles[30] revealed a new class of accessible reactive diluents, namely, benzonitriles. The reported bis(4-cyanophenyl)phenyl phosphate has proved its efficiency as a diluent,[13] but at the same time it was susceptible to hydrolysis due to the presence of the phosphate bridge.[30] In this work we introduce non-symmetrical 4-(4-cyanophenoxy)phthalonitrile (CPN) as a hydrolytically stable low-molecular weight reactive diluent containing both benzonitrile and phthalonitrile thermosetting groups. Easy processable resin blends containing CPN were prepared based on the study of rheological and thermal properties, followed by composite preparation using the solvent-free prepreg technology. Mechanical characterization and thermal aging in vacuum were performed to estimate performance of the studied composites.

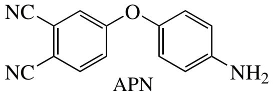
To study the effect of 4-(4-cyanophenoxy)phthalonitrile (CPN) as a diluent, formulations consisting of 1,3-bis(3,4-dicyanophenoxy)benzene (DPB) and 4-(4-aminophenoxy)-phthalonitrile (APN) as a curing agent were taken into consideration. The components DPB[31] and APN[32] were synthesized according to the published procedures. Monomer CPN was synthesized by the reaction between 4-cyanophenol and 4-nitrophthalonitrile in the presence of potassium carbonate. The product was obtained with a quantitative yield and characterized by ^{1}H and ^{13}C NMR and elemental analysis (for details, see Online Supplementary Materials).



CPN



DPB



APN

The resin components were taken in ratios of 20, 30 and 40% of CPN in the mixtures with DPB and 10% of APN to find an optimal formulation from the processability point of view. In this way, samples PN-20, PN-30, PN-30a, and PN-40 were obtained, respectively (Table 1). The DSC study demonstrated that all the prepared mixtures were amorphous (see Online Supplementary Materials, Figure S3) and uncured T_g values decreased with decreasing DPB concentration, thus demonstrating the diluenting effect of CPN. All the prepared mixtures were then investigated for rheological properties and crystallization. For resins PN-20 and PN-30 at temperatures above 100 °C it was found that 50% concentration of DPB was critical for the processing, which confirmed the previous results.[27] Since crystallization is a kinetically controlled process, DSC data showed the absence of

Table 1 Compositions of the resins studied in this work.

Resin	CPN (wt%)	DPB (wt%)	APN (wt%)	Uncured T_g/°C	Viscosity η at 130 °C/mPa s
PN-20	20	70	10	28	crystallization
PN-30	30	60	10	25	crystallization
PN-30a	30	50	20	22	106
PN-40	40	50	10	23	97

Table 2 Thermal properties of the thermosets derived from PN-30a and PN-40 after post-curing at 330 and 375 °C.

Resin	Thermoset			
	T_g/°C	$T_{5\%}$/°C (N$_2$/air)	Y_c (%)[a]	CTE[b]/10^{-6} K^{-1}
	Post-cured at 330 °C, 8 h			
PN-40	277	483/489	71	–
PN-30a	327	468/480	71	52
	Post-cured at 375 °C, 8 h			
PN-40	421	506/508	74	–
PN-30a	439	499/501	74	40

[a] Y_c is the char yield at 900 °C under N$_2$. [b] CTE is the coefficient of thermal expansion.

the crystalline phase in freshly prepared resins. However, when the blends were stirred between the cone and the heating plate of the rheometer, crystallization occurred, which resulted in disturbances in the viscosity curve shapes (Figure 1).

Resin PN-40 was cured at 180 °C in a metal mold, and then the thermoset was post-cured by free-standing at 330 °C to achieve high mechanical properties and at 375 °C for increased thermal properties.[13] The dynamic mechanical analysis (DMA) tests (Figure S7) demonstrated that the glass transition temperature of the post-cured thermosets was lower than the post-curing temperature, which meant inability of free-standing post-curing of the composite material due to devitrification of the matrix. To overcome this disadvantage, modification was made in the resin composition. Resin PN-30a contained a higher concentration of APN against CPN to facilitate curing reactions. This resin was also amorphous (Figure S3). It can be seen from Figure 1 that no crystallization was observed during viscosity measurement and the resin was post-cured under the same conditions as PN-40. The increased APN concentration in the blend provided a higher curing rate and resulted in a growth of the T_g of the thermoset up to 327 °C after post-curing at 330 °C, which allowed free-standing post-curing for the composites. Post-curing at 375 °C resulted in high thermal properties for both resins PN-30a and PN-40. This indicates a higher cross-linking degree of the thermosets, which is illustrated by higher T_g and lower CTE values in comparison with the thermosets post-cured at 330 °C (Table 2).

The TGA method was used to estimate thermal and thermal oxidation resistance of the thermosets (Figures S4, S5). The thermosets post-cured at 330 °C started to decompose ($T_{5\%}$) at temperatures around 480 °C and $T_{5\%}$ increased in both cases after post-curing at 375 °C (see Table 2). It was noticed that in air $T_{5\%}$ was higher than in nitrogen for both composites, which suggests that oxidation occurred predominantly without evolution of volatiles on an early stage. Char yields for all the thermosets were above 70%, indicating a good potential for usage as a carbon source in C/C composite fabrication.[33]

Thus, after consideration of processing properties of the resins and thermal properties of the thermosets, resin PN-30a was chosen for composite fabrication. The composites were obtained by the solvent-free prepreg technique described elsewhere.[13] Resin PN-30a was powdered in a rotary blade grinder and the resulting powder was uniformly distributed on each layer of carbon fabric with a hot iron. The preform was put in a vacuum bag and then cured in a hot-press (for details, see Online Supplementary Materials).

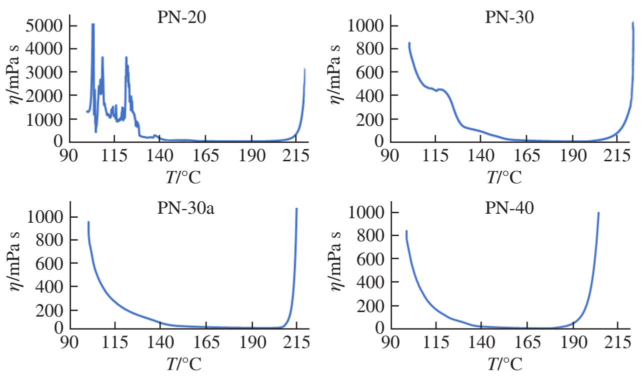


Figure 1 Viscosity profiles for the studied blends.

Composite laminates of 2 mm thickness were obtained with the resin content of 37 ± 1 wt% and cut with a CNC machine into samples for mechanical tests according to the standard procedures (Table 3). It is seen that mechanical characteristics of the composites decreased with increasing post-curing temperature. Tensile properties were predominantly determined by the fibers[34] and did not drop much for the composite post-cured at a higher temperature. At the same time, compressive strength and interlaminar shear strength (ILSS) were determined more by the matrix and the interface. It can be seen that these parameters were 1.5–2 times lower for the composite post-cured at 375 °C due to a worse mechanical performance of the matrix and transversal cracking occurring in the composites during high-temperature post-curing.[7]

Mechanical tests at elevated temperatures were performed to demonstrate the retention of mechanical characteristics of the composites. From ILSS values it is seen that the composite post-cured at 330 °C, demonstrates 92% retention of the strength at 300 °C, while the composite post-cured at 375 °C retains 100% of ILSS and tensile strength at temperatures up to 400 °C and 90% of compressive strength. It is worth noting that both composites demonstrated very low in-plane CTE values of 1.4 and 0.87×10^{-6} K^{-1}, while the previously[35] reported values for phthalonitrile carbon fiber composites was 1.97×10^{-6} K^{-1}.

Table 3 Mechanical properties of the composites with PN-30a matrices post-cured at 330 and 375 °C.

Parameter	Test method	Post-curing temperature/°C	
		330	375
Tensile strength (25 °C) σ_{11}^{+}/MPa	A	729.0 ± 27.0	643.9 ± 3.1
Tensile modulus (25 °C) E_{11}^{+}/GPa	A	62.4 ± 2.2	62.4 ± 0.7
Tensile strength (400 °C) σ_{11}^{+}/MPa	A	–	640.4 ± 15.3
Tensile modulus (400 °C) E_{11}^{+}/GPa	A	–	37.1 ± 0.4
Compressive strength (25 °C) σ_{11}^{-}/MPa	B	876.0 ± 23.5	412.8 ± 3.9
Compressive modulus (25 °C) E_{11}^{-}/GPa	B	71.1 ± 1.6	60.4 ± 0.2
Compressive strength (400 °C) σ_{11}^{-}/MPa	B	–	372.0 ± 56.3
ILSS (25 °C) τ_{13}/MPa	C	46.2 ± 2.5	33.9 ± 1.4
ILSS (300 °C) τ_{13}/MPa	C	42.7 ± 0.9	32.1 ± 0.8
ILSS (400 °C) τ_{13}/MPa	C	–	33.3 ± 2.7
CTE (in-plane)/10^{-6} K^{-1}	D	1.4	0.87

[a] Method A: GOST R 56800-2015 (ASTM D638-10). [b] Method B: GOST R 56812-2015 (ASTM D 6641). [c] Method C: GOST 32659-2014 (ISO 14130:1997). [d] Method D: GOST 57708-2017 (ASTM E228-11).

Table 4 Thermal aging of phthalonitrile composites in vacuum at 350 °C.

Post-curing temperature/°C	Mass loss (%)			ILSS/MPa			
	100 h	200 h	1000 h	0 h	100 h	200 h	1000 h
330	1.30 ± 0.11	1.69 ± 0.12	4.25 ± 0.22	46.2 ± 2.5	29.8 ± 1.2	27.7 ± 1.4	21.2 ± 2.2
375	0.51 ± 0.10	1.03 ± 0.05	2.49 ± 0.11	33.9 ± 1.4	27.6 ± 0.5	25.3 ± 0.6	17.9 ± 1.9

In recent works[8] it was shown that $T_{5\%}$ of the matrix could not serve as a criterion to estimate long-term operation temperature for the composites under oxidative conditions. In this work we decided to study the aging of composites under non-oxidative conditions. The samples for ILSS tests were sealed in glass ampules under vacuum (0.1 Torr) and placed in an oven at 350 °C for 100, 200, and 1000 h (Table 4). Every specimen was marked with a razor and mass loss along with ILSS values were estimated for each sample. It can be concluded that after 1000 h at 350 °C, pyrolysis of the matrix results in a higher mass loss of the matrix in the composite post-cured at a lower temperature, which is in accordance with the TGA data. On the other hand, an abrupt decrease of mechanical properties can be noted in the case of this composite after 100 h aging caused by further curing of the matrix at the aging temperature, which is in accordance with previously reported data.[7] After 1000 h aging, both composites retained a similar level of ILSS within the margin demonstrating that long-term pyrolysis was not dependent on the post-curing temperature in distinction to thermal oxidation.[8,9]

In summary, the use of the hybrid diluent CPN containing both phthalonitrile and benzonitrile functions made it possible to improve the processability of the resin and use the solvent-free prepreg technique to obtain composites. The mechanical tests of the obtained composites at elevated temperatures demonstrated the 90–100% retention of mechanical characteristics and preserved 50% of the strength after 1000 h aging at 350 °C.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7474.

References

1 *ASM Handbook Volume 21: Composites*, ASM International, Novelty, OH, 2001; https://www.asminternational.org/asm-handbook-volume-21-composites/results/-/journal_content/56/06781G/PUBLICATION/.

2 R. J. Iredale, C. Ward and I. Hamerton, *Prog. Polym. Sci.*, 2017, **69**, 1; https://doi.org/10.1016/j.progpolymsci.2016.12.002.

3 S. E. Evsyukov, T. Pohlmann and M. ter Wiel, in *Current Trends in Polymer Science*, Research Trends, 2020, vol. 20, pp. 1–28; https://www.researchtrends.net/tia/article_pdf.asp?in=0&vn=20&tid=2&aid=6627.

4 I. Hamerton, *Chemistry and Technology of Cyanate Ester Resins*, Springer Science & Business Media, 2012; https: //doi.org/10.1007/978-94-011-1326-7.

5 C. Uhlig, O. Kahle, O. Schäfer, D. Ewald, H. Oswaldbauer, J. Bauer and M. Bauer, *React. Funct. Polym.*, 2019, **142**, 159; https: //doi.org/10.1016/j.reactfunctpolym.2019.06.012.

6 M. Derradji, W. Jun, L. Wenbin, J. Wang and W. Liu, *Phthalonitrile Resins and Composites: Properties and Applications*, 1st edn., Elsevier, 2018; https://doi.org/10.1016/C2016-0-03991-8.

7 B. A. Bulgakov, O. S. Morozov, I. A. Timoshkin, A. V. Babkin and A. V. Kepman, *Polym. Sci., Ser. C*, 2021, **63**, 64; https://doi.org/10.1134/S1811238221010021.

8 M. S. Lobanova, V. V. Aleshkevich, A. V. Babkin, A. V. Kepman, V. V. Avdeev, O. S. Morozov and B. A. Bulgakov, *Polym. Compos.*, 2023, **44**, 8330; https://doi.org/10.1002/pc.27699.

9 M. S. Lobanova, V. V. Aleshkevich, M. Y. Yablokova, O. S. Morozov, A. V. Babkin, A. V. Kepman, V. V. Avdeev and B. A. Bulgakov, *Thermochim. Acta*, 2023, **724**, 179492; https://doi.org/10.1016/j.tca.2023.179492.

10 X. Yang, Y. Li, W. Lei, Z. Bai, Y. Zhan, Y. Li, K. Li, P. Wang, W. Feng and Q. Liu, *Polymers*, 2023, **15**, 3947; https://doi.org/10.3390/polym15193947.

11 W. J. Monzel, G. Q. Lu, T. L. Pruyn, C. L. Houser and G. T. Yee, *High Perform. Polym.*, 2018, **31**, 935; https://doi.org/10.1177/0954008318811481.

12 B.-G. Sun, Q. Lei, Y. Guo, H.-Q. Shi, J.-B. Sun, K.-X. Yang, H. Zhou, Y.-Q. Li, N. Hu, H. Wang and S.-Y. Fu, *Composites, Part B*, 2019, **166**, 681; https://doi.org/10.1016/j.compositesb.2019.02.066.

13 I. A. Timoshkin, V. V. Aleshkevich, E. S. Afanas'eva, B. A. Bulgakov, A. V. Babkin, A. V. Kepman and V. V. Avdeev, *Polym. Sci., Ser. C*, 2020, **62**, 172; https://doi.org/10.1134/S1811238220020150.

14 D. Poliakova, O. Morozov, Y. Lipatov, A. Babkin, A. Kepman, V. Avdeev and B. Bulgakov, *Polymers*, 2022, **14**, 4975; https://doi.org/10.3390/POLYM14224975.

15 M. Laskoski, A. R. Shepherd, W. Mahzabeen, J. S. Clarke, T. M. Keller and U. Sorathia, *J. Polym. Sci., Part A: Polym. Chem.*, 2018, **56**, 1128; https://doi.org/10.1002/pola.28989.

16 B. A. Bulgakov, A. V. Sulimov, A. V. Babkin, D. V. Afanasiev, A. V. Solopchenko, E. S. Afanaseva, A. V. Kepman and V. V. Avdeev, *Mendeleev Commun.*, 2017, **27**, 257; https://doi.org/10.1016/j.mencom.2017.05.013.

17 J. Yang, D. Wang, M. Li, C. Ji and B. Wang, *Composites, Part A*, 2023, **175**, 107788; https://doi.org/10.1016/j.compositesa.2023.107788.

18 D. Zhao, J. Hu, D. Wang, J. Yang, H. Zhang and B. Wang, *Compos. Sci. Technol.*, 2023, **244**, 110289; https://doi.org/10.1016/j.compscitech.2023.110289.

19 M. Wu, Y. Gu, D. Hao, X. Chen, X. Yu and Q. Zhang, *Macromol. Mater. Eng.*, 2022, **307**, 2100651; https://doi.org/10.1002/MAME.202100651.

20 B. A. Bulgakov, O. S. Morozov, I. A. Timoshkin, A. V. Babkin and A. V. Kepman, *Polym. Sci., Ser. C*, 2021, **63**, 64; https://doi.org/10.1134/S1811238221010021.

21 P. B. Dzhevakov, R. F. Korotkov, B. A. Bulgakov, A. V. Babkin, A. V. Kepman and V. V. Avdeev, *Mendeleev Commun.*, 2016, **26**, 527; https://doi.org/10.1016/j.mencom.2016.11.023.

22 M. V. Yakovlev, M. E. Kuchevskaia, V. E. Terekhov, O. S. Morozov, A. V. Babkin, A. V. Kepman, V. V. Avdeev and B. A. Bulgakov, *Mater. Today Commun.*, 2022, **33**, 104738; https://doi.org/10.1016/j.mtcomm.2022.104738.

23 G. Wang, Y. Han, Y. Guo, S. Wang, J. Sun, H. Zhou and T. Zhao, *Ind. Eng. Chem. Res.*, 2019, **58**, 9921; https://doi.org/10.1021/acs.iecr.9b01642.

24 J. Hu, H. Xie, Z. Zhu, W. Yang, W. Tan, K. Zeng and G. Yang, *Polymer*, 2022, **246**, 124745; https://doi.org/10.1016/J.POLYMER.2022.124745.

25 Y. Han, D. Tang, G. Wang, Y. Guo, H. Zhou, W. Qiu and T. Zhao, *Eur. Polym. J.*, 2019, **111**; 104; https://doi.org/10.1016/j.eurpolymj.2018.12.017.

26 W. Yin, X. Sang, J. Dong, Z. Chen and X. Chen, *High Perform. Polym.*, 2023, **35**, 618; https://doi.org/10.1177/09540083231162521.

27 B. Bulgakov, A. Sulimov, A. Babkin, I. Timoshkin, A. Solopchenko, A. Kepman and V. Avdeev, *J. Compos. Mater.*, 2017, **51**, 4157; https://doi.org/10.1177/0021998317699452.

28 M. Laskoski, J. S. Clarke, A. Neal and T. M. Keller, *Macromol. Chem. Phys.*, 2017, **218**, 1700207; https://doi.org/10.1002/macp.201700207.

29 M. V. Yakovlev, O. S. Morozov, E. S. Afanaseva, B. A. Bulgakov, A. V. Babkin and A. V. Kepman, *React. Funct. Polym.*, 2020, **146**, 104409; https://doi.org/10.1016/J.REACTFUNCTPOLYM.2019.104409.

30 V. E. Terekhov, V. V. Aleshkevich, E. S. Afanaseva, S. S. Nechausov, A. V. Babkin, B. A. Bulgakov, A. V. Kepman and V. V. Avdeev, *React. Funct. Polym.*, 2019, **139**, 34; https://doi.org/10.1016/j.reactfunctpolym.2019.03.010.

31 T. M. Keller and D. D. Dominguez, *Polymer*, 2005, **46**, 4614; https://doi.org/10.1016/j.polymer.2005.03.068.

32 H. Zhou, A. Badashah, Z. Luo, F. Liu and T. Zhao, *Polym. Adv. Technol.*, 2011, **22**, 1459; https: //doi.org/10.1002/PAT.2018.

33 V. V. Aleshkevich, B. A. Bulgakov, Y. V. Lipatov, A. V. Babkin and A. V. Kepman, *Mendeleev Commun.*, 2022, **32**, 327; https://doi.org/10.1016/j.mencom.2022.05.011.

34 R. F. Gibson, *Principles of Composite Material Mechanics*, 4th edn., CRC Press, Boca Raton, 2016; https://doi.org/10.1201/b19626.

35 J. Feng, D. Wang, J. Hu, R. Chen, J. Yang, M. Li, B. Wang and H. Peng, *J. Appl. Polym. Sci.*, 2023, **141**, e54772; https://doi.org/10.1002/app.54772.

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