Graphene oxide induced fast curing of amino novolac phthalonitrile

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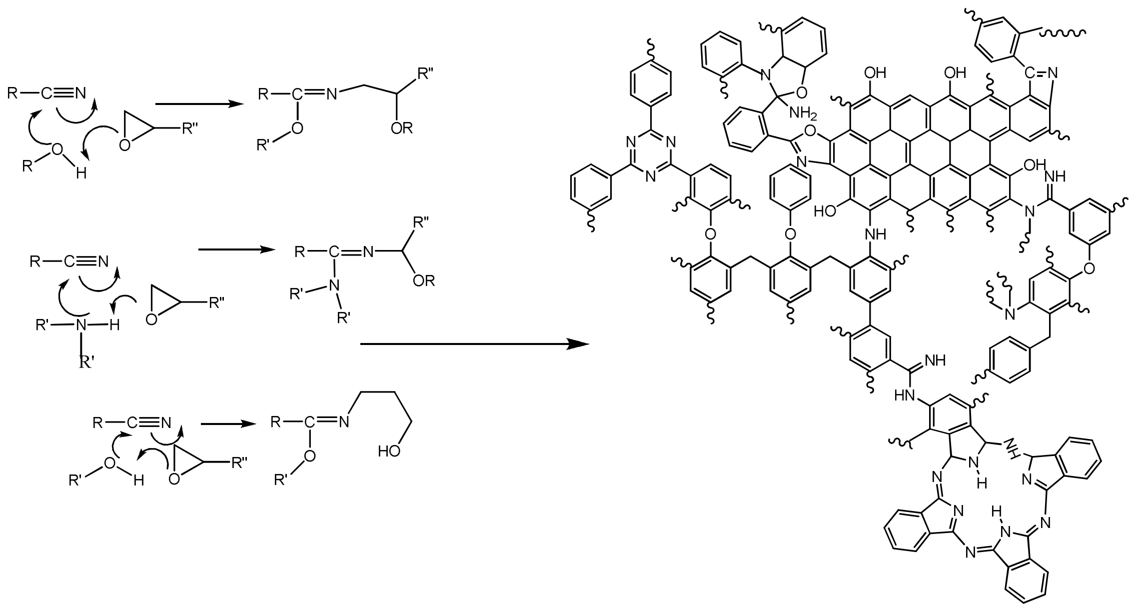
Graphical abstract

Graphene oxide reacted with amino phthalonitrile to result in a monophasic matrix with diminished Tg, wherein, the reactions of amine-epoxy, OH-CN, epoxy-CN and amine-CN not only reduced the cure temperature of phthalonitrile resin but also helped integrate the two matrices to a ductile one without any penalty in thermal stability.



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ARTICLE

Graphene oxide induced fast curing of amino novolac phthalonitrile

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Graphene oxide (GO) possessing hydroxyl and epoxy groups was synthesized by a modified Hummer's process and was found to conform to the empirical formula $C_{0.801}[\text{epoxy}]_{0.190}[\text{OH}]_{0.009}$. GO was examined as a curative for amino novolac phthalonitrile (APN). It was found to facilitate the crosslinking reaction by acting as a reactant for the amino group. Additionally, epoxy and OH groups in GO react with the nitrile groups of APN providing another pathway for facilitating the curing of APN. Epoxy groups in GO reacts with the nitrile groups of APN in presence of the OH groups (generated by the epoxy-amine reaction) facilitating the crosslinking at a lower curing temperature. Blending with GO decreases the overall curing temperature of APN. The co-reaction of the two systems led to a single phased matrix whose failure mode changed from brittle to ductile with no penalty in the thermal stability.

A. Introduction

Graphene is an atomically thick, two-dimensional material possessing superior mechanical, thermal and electrical properties. The difficulty of dispersing graphene in polymers has been solved by functionalization with groups *viz*, COOH, -OH, epoxy, isocyanate etc, which can interact with polymer chains to develop strong interfacial interactions [1-4]. Acid mediated oxidation is the preferred way to functionalize graphene to Graphene Oxide (GO) which typically contains functional groups like, epoxy, carboxyl and hydroxyl [5-10]. It has been reported that functionalized graphene could catalyze the curing processes by chemical interactions with various thermosetting matrices and affect the net-work formation and finally their properties [11-14].

Phthalonitrile, a high performance thermosetting resin has received increasing attention owing to its high glass transition temperatures (Tg), good dimensional stability, excellent moisture resistance and superior flame resistance. These features make them ideal candidate materials for marine, aerospace and electronics applications [15-17].

Phthalonitrile polymers can provide superior properties only if they are completely cross-linked. Curing of phthalonitrile polymers is a tedious process as it demands high temperature (above 300°C) and long duration (more than 20hrs) for achieving good extent of cross linking [18,19]. Various curing additives such as phenols, amines, metals, metal salts etc have been reported to facilitate the curing process of the phthalonitriles [20-24]. One effective method reported is the incorporation of amino or hydroxyl groups into the phthalonitrile units. This is achieved either by blending or by anchoring the functional groups on to the chain [20, 25, 26]. Thus, we reported a self-cure promoting amino novolac phthalonitrile (APN) in an earlier communication [27]. Reactive blending of APN resin with a refractory material like graphene oxide appeared as an effective route to increase the thermal stability of phthalonitrile resins further. To the best of our knowledge, graphene or its derivatives have not been explored as blend component for phthalonitrile polymers. In this work, the effect of GO on the curing characteristics, thermal properties and morphology of APN/GO polymer blends has been investigated and are reported for the first time.

B. Experimental

1. Materials

Graphite flakes, reagents used for oxidation of expandable graphite including potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4, 98%), sodium nitrate and hydrogen peroxide were procured from Nice Chemicals, India and were used without further purification. p-amino phenol (Sigma Aldrich), 4-nitrophthalonitirle, phenol, formaldehyde, and acetone were procured from CDH, Mumbai and were used as received.

2. Methods/ Characterization

FTIR spectra were recorded (Perkin Elmer spectrum GXA spectrophotometer) using KBr pellets in the range of 4000-400 cm^{-1}. Elemental analyses were performed using Perkin Elmer 2400 CHN Analyzer. X-Ray diffraction (XRD, Bruker D8 Discover diffractometer) was used to characterize the crystallographic structure of the samples at a scan speed 0.5s with an increment of 0.02°. Raman spectra (Witec alpha 300R confocal

Raman microscope with 532nm laser excitation) were recorded to study the functionalization and exfoliation in GO. Differential Scanning Calorimetry (DSC) was performed (TA instrument DSC Q-20) at a heating rate $10^{o}C\ min^{-1}$ in nitrogen atmosphere and thermo gravimetric analysis (TGA, TA Instruments SDT Q-600 thermogravimetric analyzer) at a heating rate of $10°Cmin^{-1}$ in nitrogen atmosphere. Transmission electron microscopy (TEM, SEI, Tecnai, T30 with EDAX,) samples were prepared by dispersing GO in water by ultrasonication and deposited on a copper grid. The microstructure of the blends was investigated using Scanning electron microscopy (SEM, Carlzeiss, EVO 50) after sputter coating with a thin layer of gold.

3. Synthesis

3.1. Synthesis of APN

APN was prepared by a two-step synthesis in which, first a novolac containing amino functionalities was synthesized. This was reacted with 4-nitrophthalonitrile to get APN [27]. The extent of amine functionalization was controlled to 20 mole %.

3.2. Synthesis of GO

GO was synthesized from graphite flakes by a modified Hummer's method [28, 29]. The product was characterized by hydroxyl and epoxy values, FTIR, Raman Spectroscopy, XRD and TEM (included in the supplementary information).

4. Preparation of APN/GO blends

The dispersion of GO in acetone (1 mg/ml) was done by bath ultrasonication at 300W for 30min at room temperature. Calculated amount of APN was then added and was dissolved in GO dispersion by mechanical stirring (610 rpm) followed by bath sonication for 5 minutes. The solvent was evaporated and the blends were vacuum dried for 4 hrs at 50°C. The blends were then cured by adopting the cure schedule: 100°C-30min, 125°C-30min, 150°C-1hr, 180°C-2hrs, 220°C-3hrs, 250°C -5hrs.

C. Results and Discussion

1. Characterization of GO

The hydroxyl and epoxy functional groups were confirmed by FTIR spectroscopy. The hydroxyl value was estimated to be 45 mg KOH/g and epoxy equivalent weight was found to be 76g/equivalent.

This amounted to an empirical formula of $C_{0.801}$ $[EPO]_{0.190}$ $[OH]_{0.009}$, where [EPO] represents epoxide groups. FTIR spectrum did not give any evidence for COOH groups. Representative structures of GO and APN are shown in Fig.1 [30]. These hydrophilic oxygen- containing functional groups provide GO sheets with good dispersibility in APN matrix.

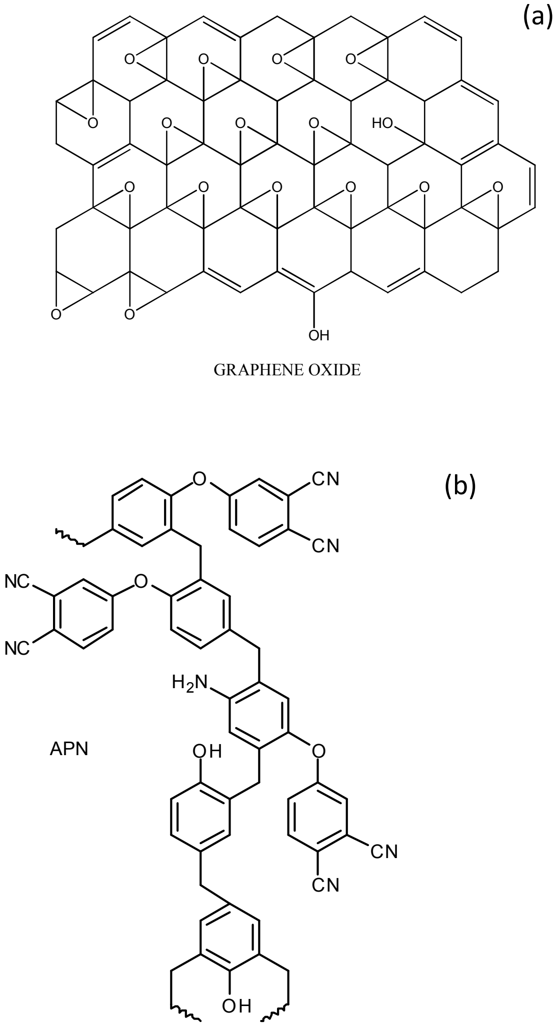


Figure1. Structure of a) GO and b) APN

2. Cure studies of APN- GO blends

APN/GO blends were prepared in varying ratios (Table 1) and were characterized for cure behavior by FTIR and DSC. The blends were also cured up to 250°C and were characterized by FTIR, TGA and SEM.

The fast curing behavior of APN/GO blends at higher proportions of GO was evidenced from the FTIR and DSC data. DSC analyses showed a cure initiation (Ti) for the blend at 122°C against 237°C for pure APN. All the blends exhibited relatively sharp exotherms centered at around 220 °C as observed in Fig 2.

Table 1 APN-GO blend compositions

Ref	APN:GO wt ratio	GO (wt %)	GO (mol %)	Effective amine-epoxy molar ratio
APN0	1:0	0	-	1:0
APN5	1:0.40	28.57	77.77	1:3.5
APN6	1:0.50	33.33	81.81	1:4.5
APN7	1:1.0	50	90	1:9
APN8	1:1.50	60	93.1	1:13.5
APN9	1:2.0	66.67	95	1:18

Table2 Cure characteristics of APN-GO blends

Ref	DSC data (°C)			ΔH for blend (J/g)
	Ti	Tp	Tf	
APN	237	330	390	110
APN5	166	214	266	178
APN6	141	211	267	270
APN7	135	210	265	452
APN8	130	210	263	492
APN9	122	207	262	669

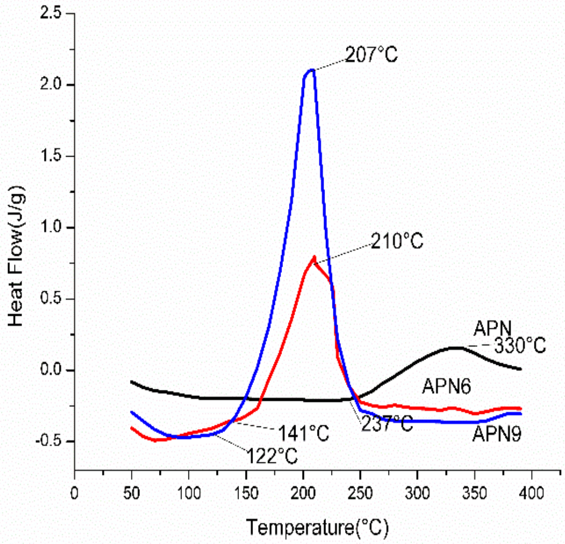
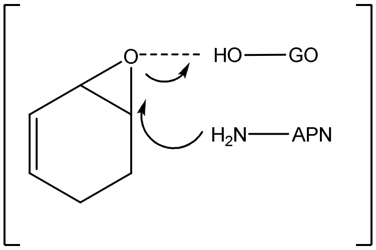


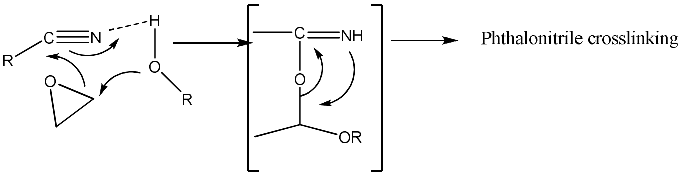
Fig 2.DSC thermograms of APN and APN-GO blends

The thermal data from DSC analyses corresponding to initiation of reaction Ti, peak cure temperature (Tp) and final cure temperature (Tf) are summarized in Table 2. An examination of the data in Table2 reveals that even at APN: GO weight ratio 1:0.4, the cure initiation temperature drifts drastically to a lower temperature of 166^{0}C. Further addition of GO causes a decrease in Ti, while the decrease in Tp and Tf is negligible. The initial part of this exotherm (Ti) signifies the epoxy-amine reaction. This was confirmed from the DSC thermogram of methylene dianiline (MDA) with an epoxy resin. The sudden decrease in Ti on adding GO to APN (*vis–a–vis* pure APN) is caused by the reaction of amine (of APN) epoxy (of GO) at a relatively lower temperature generating OH groups. At this composition (APN5), the molar ratio of amine-epoxy is 1:3.5 (exceeding 1:1). However, the Ti values decrease on further addition of GO. Since cure temperature is unaffected by a change in concentration of the reactant, the decrease can be explained by the fact that the amine - epoxy reaction is prone to be catalyzed by the OH group present on GO. Hydrogen bonding of epoxy groups by the OH group increases the electrophilicity of epoxy groups, as represented in scheme 1.

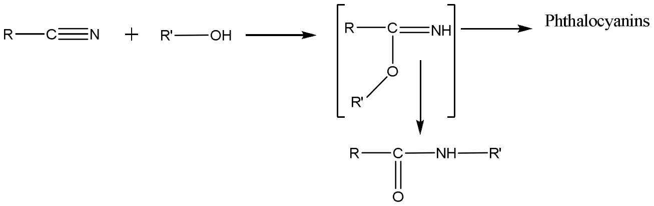


Scheme1: OH groups on GO catalyzing epoxy-amine reaction

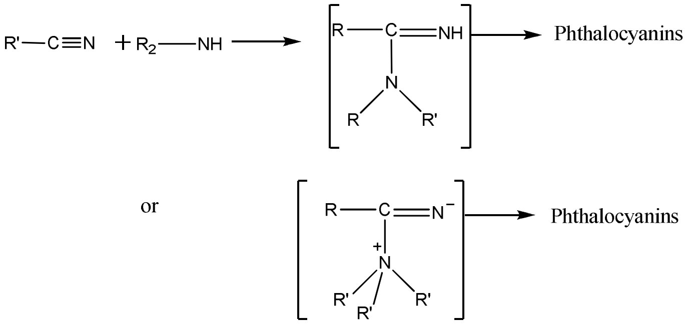
Though the Tp and Tf do not vary much, Ti value decreases systematically as explained above. The ΔH increases monotonously with increase in GO concentration. In fact, the amine-epoxy stoichiometry has already exceeded 1:1 for the composition APN5. The exotherm comprises not only of epoxy-amine reaction. The latter part of it can be caused by the epoxy-nitrile (aided by OH groups) or hydroxyl-nitrile reactions too at a higher temperature (scheme2 and 3). As the temperature regimes for this reaction are practically not affected by concentration of OH groups or epoxy groups present in GO, the temperatures (Tp and Tf) vary insignificantly. The ΔH is caused by the reaction of phthalonitrile groups with epoxy, amine and OH groups. These reactions are quite sluggish in contrast to the epoxy-amine reaction. As more of these groups (OH, epoxy) are present in compositions beyond APN5, the overall heat of reaction increases with increase in GO content. Moreover, the reaction of epoxy groups with nitrile can be catalyzed by the OH groups generated from the previous epoxy-amine reaction. Alcohol groups are known to react with the nitrile groups to give rise to the imine intermediates (scheme 3) which either undergoes further polymerization to give rise to phthalocyanines or tautomerises to the amide as per Ritter reaction [31]. The amine groups present in APN are known to add to nitrile groups thereby trigger the crosslinking [scheme 4, 37]



Scheme 2: Reaction involving epoxy- nitrile reaction aided by OH groups



Scheme 3: Reaction of nitrile group with the OH group (Ritter reaction)



Scheme 4: Reaction of amines with the nitrile group

The Tg of the fully cured materials was evaluated by DSC analysis and was found to be in the range of 300-310°C (fig 3). Thus, the GO diminishes the Tg of APN from 400°C to 310°C (APN9) confirming the reaction between them. In the absence of any co-reaction between APN and GO, two distinct Tg (i.e. for GO and cured APN) should have been detected. A single Tg transition confirms integration of GO with APN.

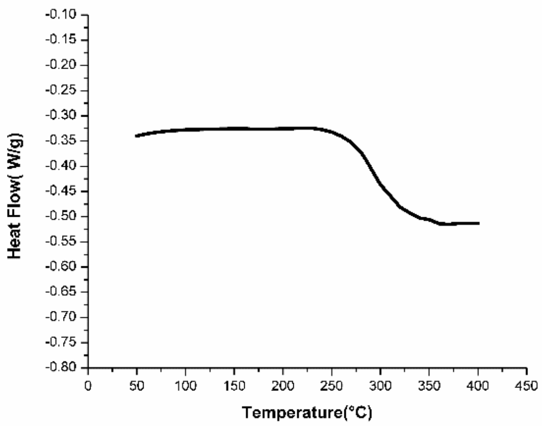


Fig 3.DSC thermogram showing the Tg of APN9 (cured)

Literature reports the curing of biphenyl phthalonitrile monomers catalyzed by bis[4-(4-aminophenoxy)phenyl] sulfone (p-BAPS) exhibiting an exothermic transition at 260°C corresponding to triazine ring formation by the cyclotrimerization of nitrile groups [32,33,34,35]. A blend of the same system with diglycidyl ether of bisphenol A exhibited two exothermic transitions attributed to the reaction of epoxy resin with amine groups in p-BAPS and to the thermal degradation/ decomposition of the polymer and/or excess epoxy resin, respectively. Reactions of epoxy groups with the phthalonitrile derivative of p-aminophenol have also been reported by H.Guo et.al. [35]. The reaction was characterized by a two-step cure pattern, attributed to the co-reaction of epoxy-amine and amine-nitrile functions with cure initiation temperatures around 180°C and 296°C respectively.

In the present system, an almost single stage curing of APN with GO was observed, which might form triazine, phthalocyanine rings, oxazloidones etc as demonstrated by FTIR spectra. The probable products of APN-GO blends formed by diverse reactions involving epoxy- amine, amine-nitrile, epoxy-nitrile, and OH-nitrile are shown in Fig 4. The intermediate compounds are shown in schemes 2, 3 and 4.

The FTIR spectra of uncured APN, cured APN and a typical cured APN-GO blend (1:1) are shown in Fig 5.It is evidenced that near complete conversion of the nitrile group was achieved for all the blends containing GO. To establish the possible mechanisms, the reaction between an aliphatic epoxy and APN (1:1 molar) was examined separately under dynamic temperature ramping conditions. The conversion of nitrile group (by nitrile- epoxy reaction, refer scheme 2) in this case was only 20%. Phenolic, epoxy and amino groups catalyzing the crosslinking of APN has been previously reported from this lab (26, 27, 37). Hence, a mechanism involving both hydroxyl and epoxy groups reacting with the nitrile group (scheme 2 and scheme 3) appear to be possible for explaining the accelerated curing of APN, leading to complete conversion of nitrile groups. The OH groups generated in the epoxy-amine reaction are also available for the reaction. It may be noted that these reactions are only prelude to the cyclisation reactions of phthalonitrile that ultimately give rise to poly phthalocyanines, indoline etc.

The FTIR spectra of the cured blends revealed that the characteristic absorption peak of the nitrile group (2230 cm^{-1}) in APN decreased and the epoxy group (916cm^{-1}) absorption in GO disappeared with incorporation of more GO. The peak appearing at 1365 cm^{-1} is assigned to the triazine groups. However, the absorption due to other probable products including phthalocyanin, oxazoline and isoindoline, could not be distinctly identified due to overlap of the peaks in FTIR.

The residual nitrile content for cured APN was quantitatively estimated to be around 84% in the absence of GO. This was quantified by FTIR spectroscopy using the absorption peak at 2230 cm^{-1} (due to $C\equiv N$ group) with the peak at 1220 cm^{-1} (due to C-O-C stretching) as the reference peak. The minimum loading of GO required for the complete conversion of the nitrile groups is estimated to be in the range of 20-30 wt%

of GO. The conversion achieved for APN with different GO content is shown in Fig 6.

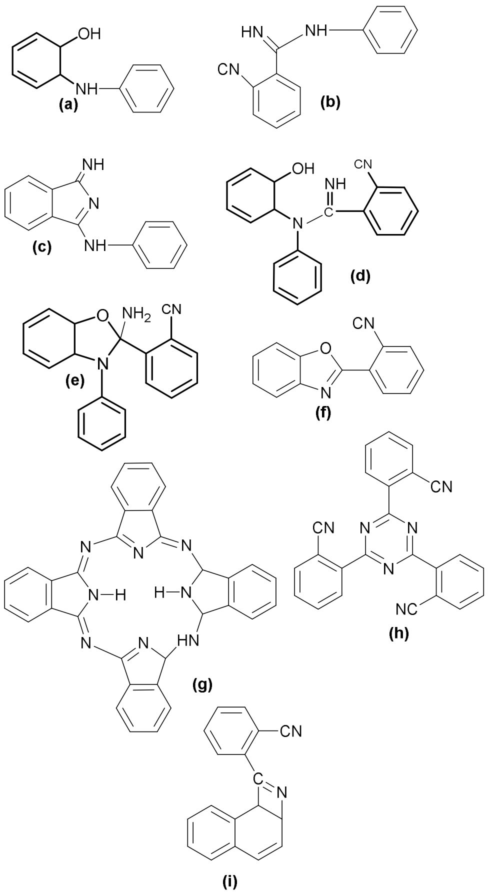


Fig 4 Probable reaction intermediates of APN-GO blends

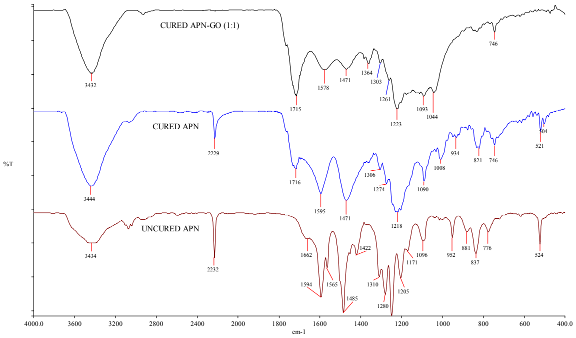


Fig 5. FTIR spectrum of uncured APN, cured APN and APN-GO (1:1) blend

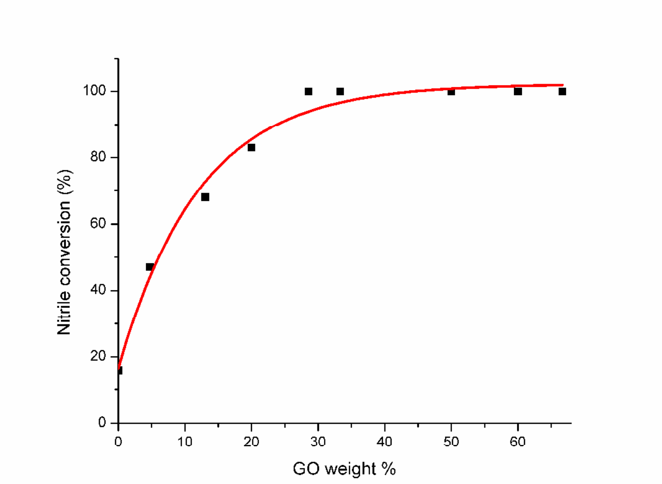


Fig 6. Variation of nitrile conversion with GO content

As per Fig 6, under the cure condition employed, phthalonitrile curing is dependent on epoxy concentration. It is seen that complete nitrile conversion occurs when amine-epoxy molar ratio exceeds 1:3.5 (APN5, Table2). At this molar ratio, the amine-epoxy reaction leaves behind ~ 2.5 equivalents of unreacted epoxy, 1 equivalent of OH (from amine-epoxy reaction) and 1 equivalent of 2° or 3° amine, as the case may be. This accounts for a total of 4.5 equivalents of reactants which can react with nitrile groups at high temperatures. This also implies that 1 phthalonitrile moiety requires at least 1mole of either hydroxyl or epoxy or amine groups for its conversion.

3. Thermal decomposition of cured APN-GO blends

Cross linked networks of epoxy – amino phthalonitrile systems are reported to exhibit good thermal, thermo-oxidative stability and high char yield [36].

Table 3 Thermal properties of typical APN-GO blends (from TGA)

Ref	T_i (°C)	T_p (°C)	Char yield at 900 °C Y_c(%)
APN	420	580	79
GO	161	220	52
APN5	425	580	78
APN9	450	582	80

The TGA results compiled in Table 3 show that the thermal stability of the cured blends are unaffected by GO modification, though GO as such decomposes at lower temperature (~160°C) and that it generates aliphatic groups in the matrix.

4. Morphology of the blends

Fig 7 shows the SEM image of freshly fractured surfaces of cured APN-GO blends (fractured in liquid nitrogen). The samples show plate like morphology with reasonably good dispersion of GO throughout the matrix (Fig 7(a)). GO has a flaky texture. At high GO loading, its layered microstructure is seen in Fig. 7(b). The compositions with higher GO content exhibit a ductile-like fracture pattern, showing more plastic deformation characteristics. This is advantageous for gaining toughness for the matrix of APN based composites that are generally brittle.

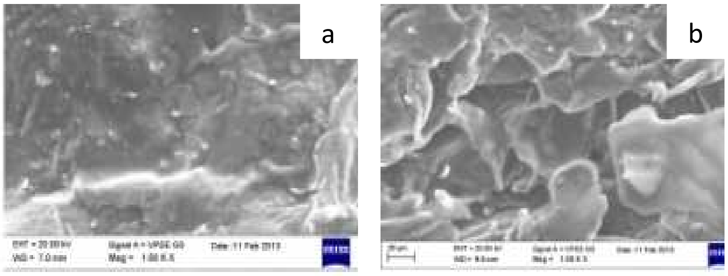


Fig 7. SEM images of a) APN5 and (b) APN8

Conclusions

Graphene oxide, bearing epoxy and hydroxyl functionalities were synthesized and characterized. Studies on the curing of amine functionalized novolac phthalonitrile in presence of GO revealed two major influences of GO on APN i.e., lowering of curing temperature by about 100°C and the achievement of complete conversion of nitrile groups. During the cure reaction, the epoxy groups of GO underwent ring opening by the amino groups, in addition to its reaction with the nitrile groups in phthalonitrile. The nitrile group reacts with OH, epoxy and NH groups present in the system causing an overall diminution in cure temperature. These reactions generated structures like oxazolidones, phthalocyanins, triazine etc in the cured matrices. The cured blends showed a single phase morphology without any penalty in thermal stability. Blending with GO decreased the Tg of APN. Morphology of the cured APN-GO blends showed reasonably good dispersion of GO in APN having a ductile fracture at higher GO loading.

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1. G.Wang, J.Yang, J.Park, X.Gou, B.Wang, H.Liu,etal.*Facile synthesis and characterization of graphene nanosheets. J.PhysChem, 2008*; 112: 8192–5.
2. R. D. Dreyer,S.Park, C. Bielawski W.,R. S. Ruoff*The chemistry of graphene oxide*, *ChemSoc Rev,* 2010; 39:228–40.
3. T. Ramanathan, A.A. Abdala, S. Stankovich, D.A. Dikin, M.H.Alonso, R.D.Piner, etal. *Functionalized graphene sheets for polymer nanocomposites*. *Nat Nanotechnol,* 2008; 3: 327, 31.
4. Y.Geng,S. J Wang, J.K.Kim, *Preparation of graphite nanoplatelets and graphene sheets. J. Colloid Interface Sci,* 2009; 336:592–8.
5. T. Szabo, O. Berkesi, L. Dekany, *Drift study of deuterium-exchanged graphite oxide. Carbon*, 2005; 43(20):3186–93.
6. A.B. Bourlinos,D. Gournis, D. Petridis, T. Szabo, A.Szeri,I.Dekany*Graphite oxide: chemical reduction to graphite and surface modification with primary aliphatic amines and amino acids. ChemMater* 2003; 19:6050–5.
7. E.Bekyarova, M.E.Itkis, P.Ramesh, C.Berger, M.Sprinkle, W.A.Herr, et al. *Chemical modification of epitaxial graphene: spontaneous grafting of aryl*

groups American ChemSoc 2009; 131:1336–7.

8. C.Shan,H.Yang, D. Han,Q.Zhang ,A. Ivaska,L.Niu, *Water soluble graphene covalently functionalized by biocompatible poly- l-lysine. Langmuir,* 2009; 25:12030–3.
9. H.C.Schniepp, J. L.Li,M.J. McAllister,H. Sai,M. H. Alonso, D. H. Adamson, et al. *Functionalized single graphene sheets derived from splitting graphite oxide .J PhysChem C,*2006;110:8535–9.
10. L. R.Radovic, A. B.Silva-Tapia, Vallejos-F.Burgos, *Oxygen Migration on the Graphene Surface, Origin of Epoxide Groups. Carbon,* 2011, 49, 4218−4225.
11. D.Cai, M. Song *Recent advance in functionalized graphene/polymer nanocomposites. J Mater Chem,* 2010; 20(37):7906–16.
12. M.Fang, Z.Zhang, J.Li, H.Zhang, H.Lu, Y. Yang, *Constructing hierarchically structured interphases for strong and tough epoxy nanocomposites by amine-rich graphene surfaces. J Mater Chem*, 2010; 20(43):9635–43.
13. X.Zhao, Q.Zhang,D.Chen, *Enhanced mechanical properties of graphene-based poly (vinyl alcohol) composites. Macromolecules,* 2010; 43:2357–63.
14. M.A.Rafiee, J.Rafiee, Z.Wang, H.Song, Z.Yu, N.Koratkar *Enhanced mechanical properties of nanocomposites at low graphene content. ACS Nano,* 2009; 3(12):3884–90.
15. T.M.Keller. *Phthalonitrile-based high temperature resin. J Polym Sci Part: A PolymChem,* 1988; 26: 3199–3212.
16. T.M.Keller. *Imide-containing phthalonitrile resin. Polymer*, 1993; 34: 952–955.
17. P.M.Hergenrother. *The use, design, synthesis, and properties of high performance/high temperature polymers: an over-view. High Perform Polym*, 2003; 15: 3–45.
18. D.D. Dominguez and T.M. Keller *Low-melting phthalonitrile oligomers: preparation, polymerization and polymer proper-ties. High Perform Polym*, 2006; 18: 283–304.
19. M. Laskoski, D.D. Dominguez and T.M.Keller. *Synthesis and properties of a bisphenolA based phthalonitrile resin. J PolymSci Part: A PolymChem*, 2005; 43: 4136–4143.
20. M.J.Sumner, M.Sankarapandian, J.E. McGrath, J.S.Riffle and U.Sorathia, *Flame retardant novolac–bisphthalonitrile structural thermosets. Polymer,* 2002; 43: 5069–5076.
21. D.D. Dominguez, H.N.Jones and T.M.Keller. *The effect of curing additive on the mechanical properties of phthalonitrile-carbon fiber composites.Polym Composites,* 2004; 25: 544–561.

22. S.B.Sastri and T.M.Keller. *Phthalonitrile cure reaction with aromatic diamines. JPolym Sci Part: A Polym Chem,* 1998; 36: 1885–1890.
23. S.B.Sastri and T.M.Keller. *Phthalonitrile polymers: cure behavior and properties. JPolymSci Part: A PolymChem,* 1999; 37: 2105–2111.
24. X.L.Yang, and X.B.Liu, *Study on curing reaction of 4-amino-Phenoxyphthalonitrile/bisphthalonitrile. Chem Lett,* 2010; 21: 743–747.
25. K.Zeng, H.B.Hong, S.H.Zhou, D.M.Wu, P.K.Miao, Z.F.Huang, et al. *A new soluble aramide with pendant phthalonitrile units and polymer property enhancement by nitrile cure reactions polymer.Polymer,*200950: 5002–5006
26. Dhanya Augustine, Dona Mathew, C.P. Reghunadhan Nair, *Phenol-containing phthalonitrile polymers: synthesis, cure characteristics and laminate properties. Polymer International,* 2013: 1068-1076.
27. Dhanya Augustine, K.P. Vijayalakshmi, R. Sadhana, Dona Mathew, C.P. Reghunadhan Nair, *Hydroxyl terminated PEEK-toughened epoxy–amino novolac phthalonitrile blends – Synthesis, cure studies and adhesive* properties, Polymers, 2014 10.1016/j.polymer.2014.09.042.
28. W. S. Hummers and R. E. Offeman, Preparation of Graphitic Oxide J. Am. Chem. Soc., 1958, 80, 1339.
29. D. Li, M. B. Muller, S. Gilje, R. *Processable aqueous dispersions of graphene nanosheets, Nature Nanotechnology,* 2008
30. Riccardo Salvio, et.al. *The Formation of Large-Area Conducting Graphene-Like Platelets, Chem. Eur. J.* 2009, 15, 8235 – 8240.
31. Jerry March, Advanced Organic Chemistry. *Reactions, Mechanism and structure*, 4th edition, Wiley Interscience Publication, New York, 1992, pp-970.
32. Dawn D. Dominguez, Teddy M. Keller *Phthalonitrile-epoxy blends: Cure behavior and copolymer properties, 2008 Wiley Periodicals, Inc. J Appl Polym Sci* 110: 2504–2515, 2008
33. Keller, T. M., *Phthalonitrile-based high temperature resin, J Polym Sci Part A: Polym Chem* 1988, 26, 3199.
34. Keller, T. M., *Synthesis and Polymerization of Multiple Aromatic Ether Phthalonitriles, Chem Mater* 1994, 6, 302.
35. Sastri, S. B.; Armistead, J. P.; Keller, T. M., *Phthalonitrile-carbon fiber composites, Polym Compos* 1996, 17, 816.
36. Heng Guo, Yanke Zou, Zhiran Chen, Jiandong Zhang, Yingqing Zhan, Jian Yang and Xiaobo Liu, *Effects of self-promoted*

curing behaviours on properties of phthalonitrile/epoxy copolymer, High Performance Polymers, 2102 1-9.

37. Dhanya Augustine, Dona Mathew C.P. Reghunadhan Nair, *End-functionalized thermoplastic-toughened phthalonitrile composites: influence on cure reaction and mechanical and thermal properties, Polymer International,* 2014.