

Phenolic-Epoxy Matrix Curable by Click Chemistry—Synthesis, Curing, and Syntactic Foam Composite Properties

Kayyurkarathi Sunitha, Dona Mathew, Chethrappilly Padmanabhan Reghunadhan Nair

Polymers and Special Chemicals Group, Vikram Sarabhai Space Centre, Thiruvananthapuram 695 022, India

Correspondence to: C. P. Reghunadhan Nair (E-mail: cprnair@gmail.com)

ABSTRACT: Alkyne functional phenolic resin was cured by azide functional epoxy resins making use of alkyne-azide click reaction. For this, propargylated novolac (PN) was reacted with bisphenol A bisazide (BABA) and azido hydroxy propoxy novolac (AHPN) leading to triazole-linked phenolic-epoxy networks. The click cure reaction was initiated at 40–65°C in presence of Cu_2I_2 . Glass transition temperature (T_g) of the cured networks varied from 70°C to 75°C in the case of BABA-PN and 75°C to 80°C in the case of AHPN-PN. DSC and rheological studies revealed a single stage curing pattern for both the systems. The cured BABA-PN and AHPN-PN blends showed mass loss above 300°C because of decomposition of the triazole rings and the novolac backbone. Silica fiber-reinforced syntactic foam composites derived from these resins possessed comparable mechanical properties and superior impact resistance vis-a-vis their phenolic resin analogues. The mechanical properties could be tuned by regulating the reactant stoichiometry. These low temperature addition curable resins are suited for light weight polymer composite for related applications. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41254.

KEYWORDS: catalysts; composites; rheology

Received 24 March 2014; accepted 29 June 2014

DOI: 10.1002/app.41254

INTRODUCTION

For the past decades, advanced composites have become main structural materials of aviation and aerospace industries.¹ Among these composite materials, much attention is paid to low temperature molding materials with high performance. Phenolic resins are widely used as matrix resin in polymer composites.^{2–5} It is a known hardener for epoxy resins and a matrix resin in ablatives and thermal protection systems.^{6,7} Owing to the good thermo-oxidative stability, moderate mechanical properties, and low cost, phenolic resins have found an unprecedented place in aerospace industry in applications such as high performance thermal protection systems for nose caps and exit cones of rocket nozzles, light weight thermal protection systems for re-entry capsules etc.⁸ However, the condensation cure reaction of phenolics with concomitant evolution of volatiles creates voids in cured products, impairing their mechanical properties.

Novolac cured epoxy resin system constitutes an addition curable formulation. But they need high curing temperature as the phenol-epoxy reaction is quite sluggish even on catalysis.⁹ In this background, we explored click chemistry for effecting the curing of novolac by reaction with epoxy.

Click chemistry forms a powerful palette of bond forming reactions that has already proven in the field of polymers and

material synthesis.^{10–15} It enables engineering of highly diverse building blocks in high yields and with no byproducts.^{16–22} Since azides and alkynes are readily attached to a variety of molecular scaffolds, the Huisgen's 1, 3-dipolar cycloaddition involving them offers an easy route for altering the cure mechanism of many polymer systems. In this article, we report the synthesis and characterization of click-curable phenolic and epoxy resin systems. The matrix nature of the resin was validated by processing syntactic foams.

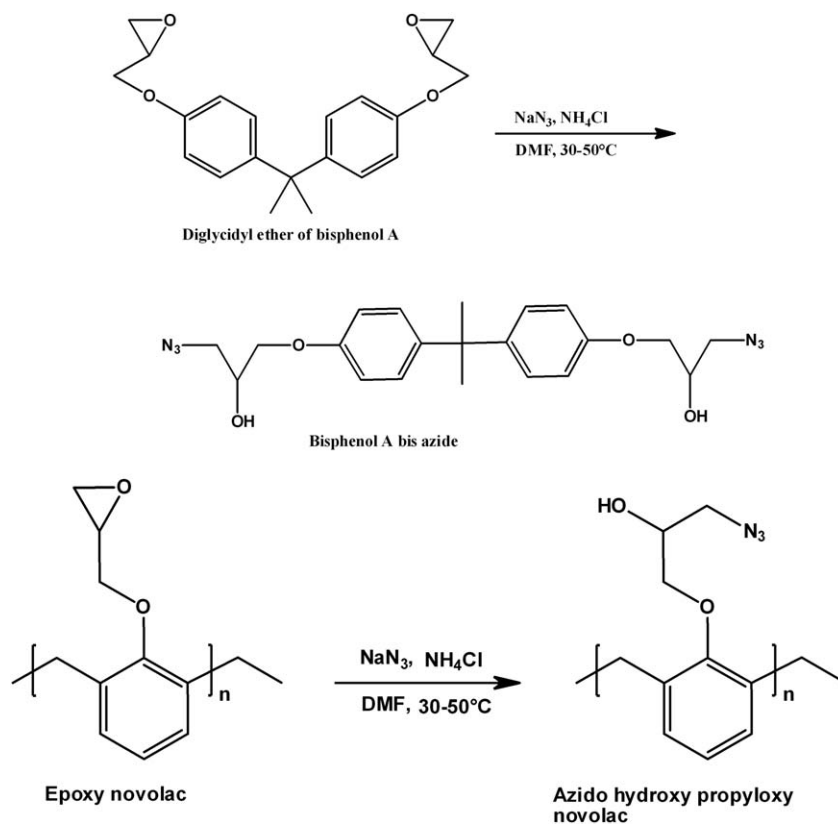
EXPERIMENTAL

Materials and Methods

Epoxy novolac and diglycidyl ether of bisphenol A were procured from Huntsman India, Bangalore, and were used as such. Sodium azide (SRL Mumbai, 99%), ammonium chloride (SRL Mumbai, 99%), and dimethyl formamide (SRL Mumbai, 99%) were used as received. The low density glass microballoon fillers, k-37 and k-25 were supplied by 3M Company, USA. Silica fiber (silica content 99%) in the form of chopped strands of length 4–7 mm procured from M/s.Valeth High Tech composites, Chennai, India, was used as such. The fibrils had an average diameter of 16 μm .

Characterization

NMR spectra were recorded on a Bruker Avance spectrometer (300 MHz) using CDCl_3 as solvent. FT-IR spectra were recorded



Scheme 1. Synthesis of BABA and AHPN.

using Perkin Elmer spectrum GX spectrophotometer at a resolution of 4 cm^{-1} . DSC analysis was conducted using a TA instruments model 2920 modulated DSC at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 . Dynamic mechanical analysis (DMA) was carried out using DMA Q800 (TA Instruments, USA) in a 35 mm dual cantilever mode at a heating rate of $3^\circ\text{C}/\text{min}$ at 1 Hz. Thermogravimetric analysis (TGA) was done on a TA instruments, model SDT-2960 simultaneous DTA (differential thermal analysis) -TGA at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 .

Rheological characterization was done with a Stress Tech Rheologica rheometer using a 20 mm parallel plate assembly in oscillation mode at a frequency of 1 Hz and strain of 1%. The gap between the plates was maintained at 0.5 mm.

Synthesis of Bisphenol A Bisazide and Azido Hydroxy Propoxy Novolac

Bisphenol A bisazide (BABA) was synthesized by a reported procedure.²³ For the synthesis of azido hydroxy propoxy novolac (AHPN), epoxy novolac (5 g), sodium azide (1.53 g), ammonium chloride (1.34 g), and dimethyl formamide (50 mL) were introduced into a 100 mL round bottom flask. The reaction flask was covered with dark cloth and the reaction was continued at 30°C for two days and at 50°C for 8 h. The reaction mixture was poured into water and the product was extracted with diethyl ether and washed several times with water. The solvent was evaporated off and the product was dried under vacuum at room temperature for 16 h (yield = 4.5 g). The product was characterized by FTIR and ^1H NMR spectroscopies.

Synthesis of Propargylated Novolac

Propargylated novolac (PN) was synthesized from novolac resin according to a previously reported procedure.²⁴ Novolac resin (100.0 g) dissolved in acetone and potassium carbonate (182.0 g) and benzyl triethyl ammonium chloride (3.0 g) were added into a 500 mL RB flask and reaction temperature was set at 60°C . Subsequently, propargyl bromide (98.0 mL) was introduced into the mixture drop by drop and stirring continued for

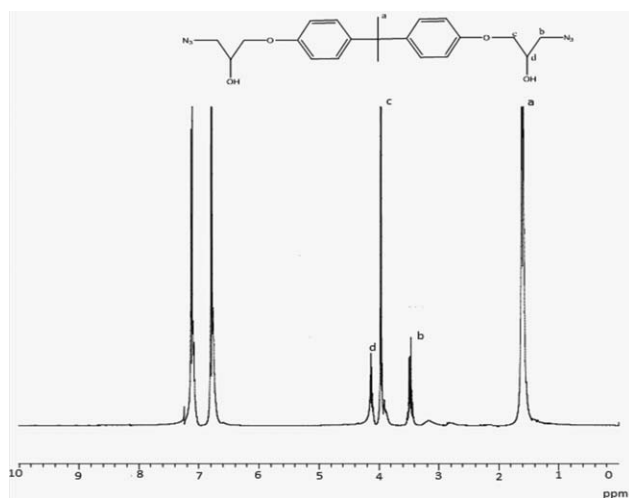
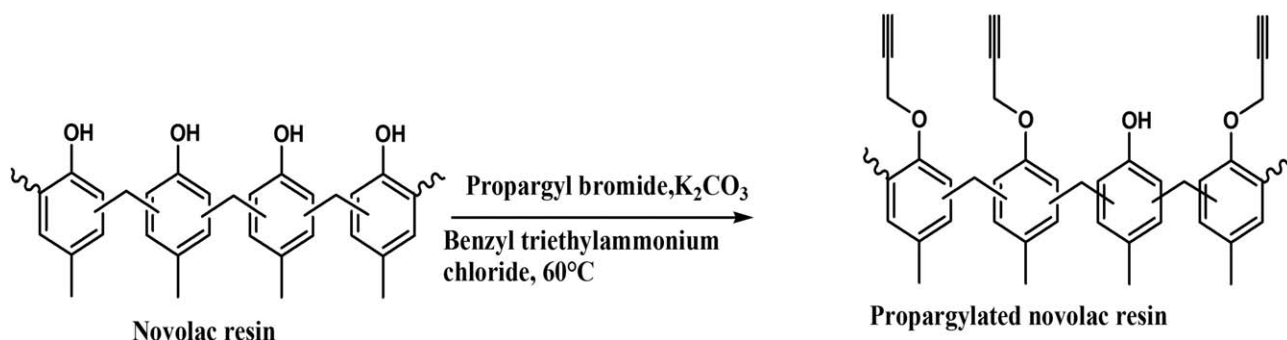


Figure 1. Proton NMR spectrum of bis phenol A bisazide.



Scheme 2. Synthesis of propargylated novolac (PN).

35 h. The mixture was filtered; filtrate was concentrated, dried at 70°C under vacuum for 24 h, and characterized by ¹H NMR and FTIR.

Coupling of (AHPN-PN) and (BABA-PN) via Click Reaction

Click coupling involving PN and BABA/AHPN was done in varying azide concentrations (41, 44, 47, 50 mol %). The two resins were mixed by dissolving them together in acetone in the presence of Cu₂I₂ catalyst (0.1 wt % of the monomer) and driving off the solvent in vacuum. The curing of the mixture was then carried out at 120°C for 16 h. Curing of the noncatalyzed system was performed under identical conditions.

Processing of Composites

Syntactic foam composites of dimension 100 mm × 100 mm × 30 mm were processed using the AHPN-PN and BABA-PN resins with different azide concentrations (41, 44, 47, 50 mol % of propargyl groups). AHPN-PN or BABA-PN and catalyst were dissolved in acetone (50 mL) and mixed with chopped silica fiber in a beaker till all the fibers were well dispersed and wet with the resin. Required quantity of microballoons k 25 and k 37 was then added and thoroughly mixed to get a uniform dispersion. Mixing was done gently to avoid breaking of fibers and microballoons. This method of addition of fiber followed by addition of microballoon has been reported to lead to better mechanical performance for fiber-reinforced syntactic foams.^{25,26} The mixture was then placed in a mould of dimension (100 mm × 100 mm × 30 mm) and heated at 60°C for 8

h and at 120°C for 8 h. Density of the syntactic foams was determined from the mass and dimensions. For comparison, resole-phenolic resin based syntactic foams were also processed in similar lines, adopting a cure schedule of 125°C—30 min, 150°C—1 h and 180°C—2 h. Mechanical properties were determined using an INSTRON UTM 4202, as per ASTM standards D695 and D256, respectively, for compressive strength (specimen dimension 13 mm × 13 mm × 25.4 mm; crosshead speed: 1.3 mm/min) and resilience (specimen dimension 64 mm × 13 mm × 3 mm; crosshead speed: 3.16 m/s).

RESULTS AND DISCUSSION

Synthesis of Clickable Resins and Curing to Triazole Networks

BABA was synthesised from diglycidyl ether of bisphenol A with sodium azide, while azido hydroxy propoxy novolac was synthesized from novolac epoxy by the same reaction as shown in Scheme 1. They were characterized by ¹H NMR (300 MHz, d₆-acetone). Typical proton NMR of BABA is given in Figure 1. AHPN showed similar signals in its NMR spectrum.

BABA; δ (ppm); 2.0 (s, —(CH₃)₂), 3.5 (m, 2H, CH₂—N₃), 4 (d, 2H, O—CH₂), 4.2 (m, 1H, CH—OH), 6.8–7.2 (—Ar)

AHPN; δ (ppm) = 3.8 (broad, Ar—CH₂—Ar), 3.47 (m, 2H, CH₂—N₃), 3.99 (d, 2H, O—CH₂), 4.15 (m, 1H, CH—OH), 6.82–7.12 (—Ar).

FTIR (KBr, cm⁻¹): 2102 (azide), 3379 (—OH)

NMR and IR spectra conformed to the expected structure for both compounds.

Epoxy value after azidation (less than 0.01%) and the absence of the characteristic epoxy peak at 915 cm⁻¹ confirmed complete conversion of epoxy group to azide both in AHPN and BABA.

PN was synthesized as shown in Scheme 2 and characterized by IR, ¹H NMR, and hydroxyl value.

The signal at 3.45 ppm in proton NMR accounted for propargyl group (≡C—H) in the PN oligomer.²⁴ The —OCH₂ groups were noted at 4.6–4.9 ppm range while the aromatic protons appeared at 6.9–7.1 ppm. The CH₂ bridge appeared as a broad signal at around 3.9 ppm. NMR of PN is shown in Figure 2. FTIR spectrum showed characteristic absorption at 3288 and

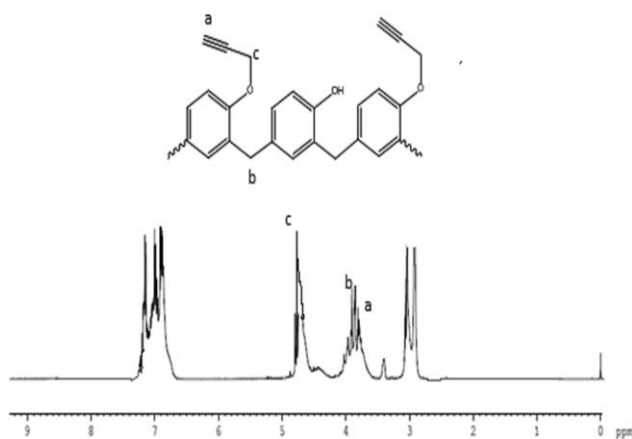
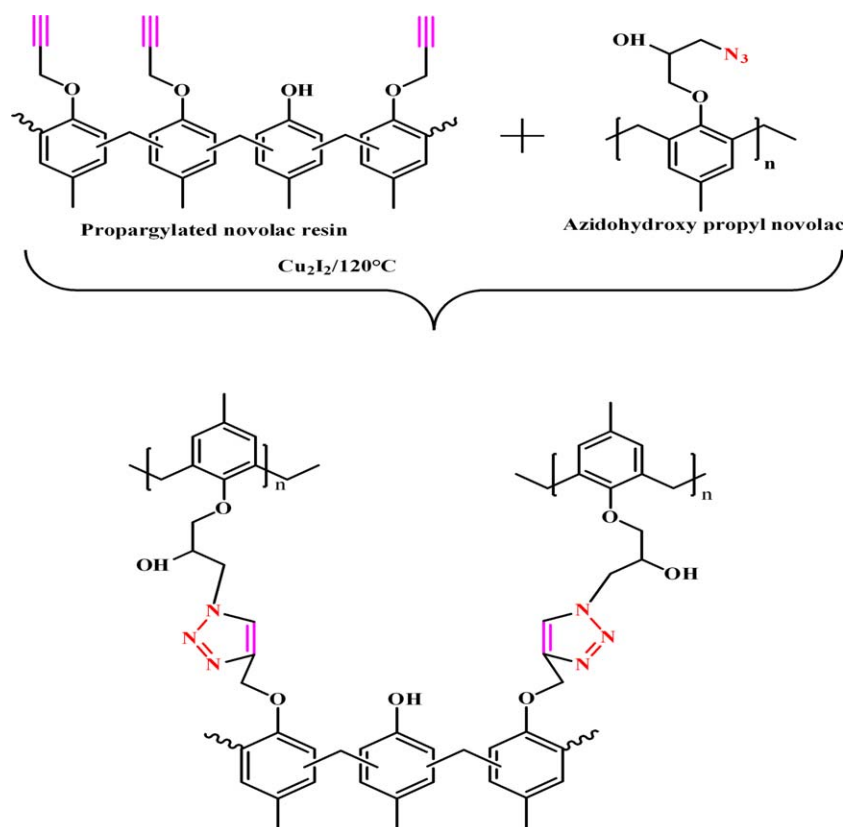


Figure 2. Proton NMR spectrum of Propargylated novolac.



Scheme 3. Click reaction between Phenolic novolac resins bearing azide and propargyl groups leading to phenolic triazole network. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2230 cm^{-1} corresponding to ($\equiv\text{C}-\text{H}$) and ($\text{C}\equiv\text{C}$) groups, respectively, and a less intense peak at 3424 cm^{-1} because of residual $-\text{OH}$ groups present. Extent of propargylation was estimated as 85% as inferred from the hydroxyl value of the resin (62 mg KOH/g) after propargylation.

Cure Reaction of AHPN and PN

BABA and O-PN were coupled via the click reaction utilizing the reaction between the azide and propargyl groups.²⁴

Similarly, azido hydroxyl propoxy novolac and PN were coupled via click reaction as per Scheme 3. Cross-linking/coupling of azido and propargyl groups occur through 1, 2, 3 triazole ring formation.^{27–30} The cure reaction of AHPN-PN systems was monitored using FTIR, DSC, and rheometry. Before curing, FTIR spectrum of AHPN-PN blend exhibited well-defined absorption at 2102 cm^{-1} because of the presence of

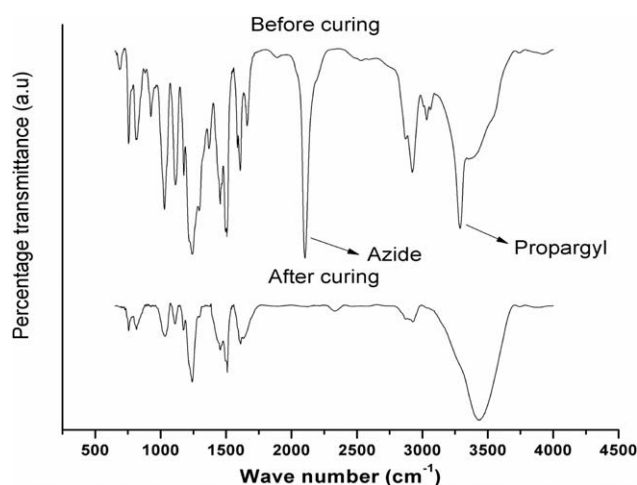


Figure 3. FTIR spectra of AHPN-PN (1:1) before and after click curing.

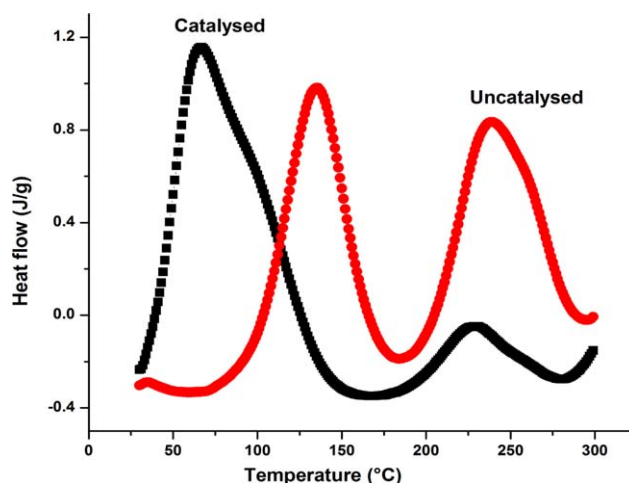


Figure 4. DSC traces of catalyzed and uncatalyzed “click” reaction of AHPN-PN system (heating rate- $10^\circ\text{C}/\text{min}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

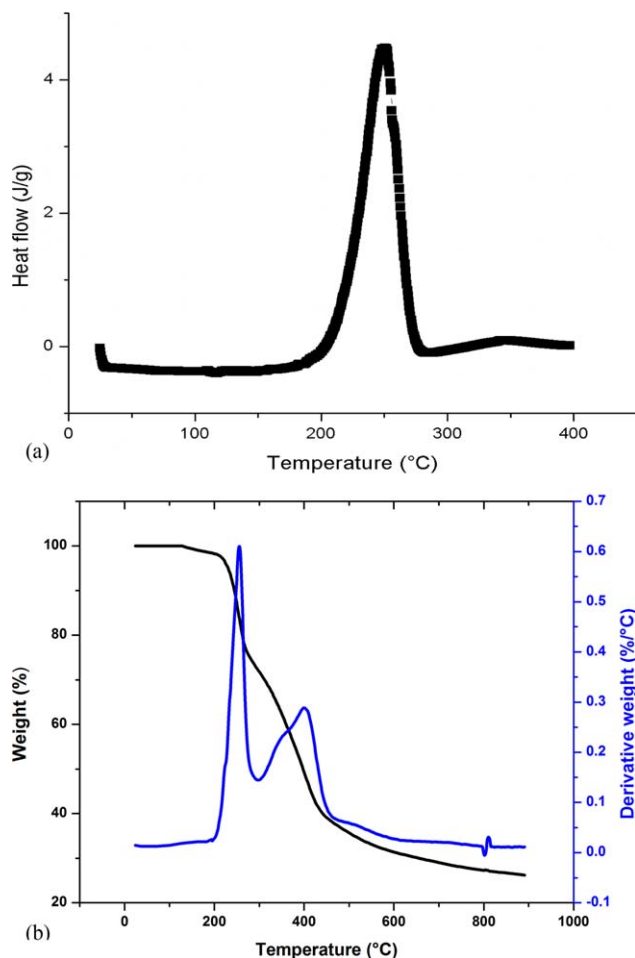


Figure 5. DSC traces for the catalytic decomposition of AHPN (10°C/min). b) TGA of AHPN (10°C/min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

azide groups in AHPN and also characteristic absorptions of PN resin at 3288 cm^{-1} ($\equiv\text{C-H}$) and 2230 cm^{-1} ($\text{C}\equiv\text{C}$) as shown in Figure 3.

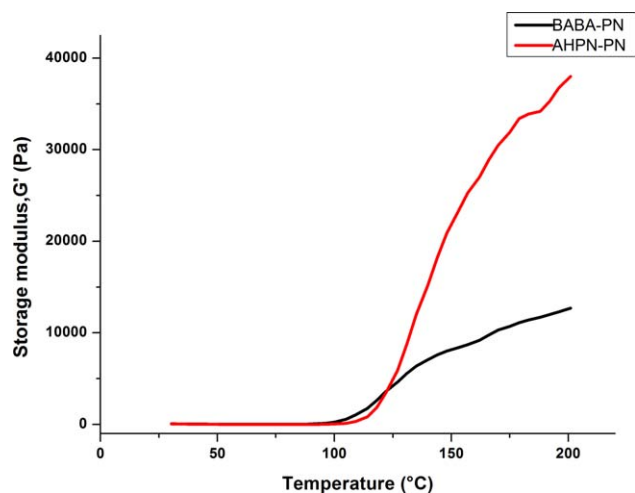


Figure 6. Variation in storage modulus with temperature for BABA-PN and AHPN-PN (uncatalyzed), heating rate 5°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

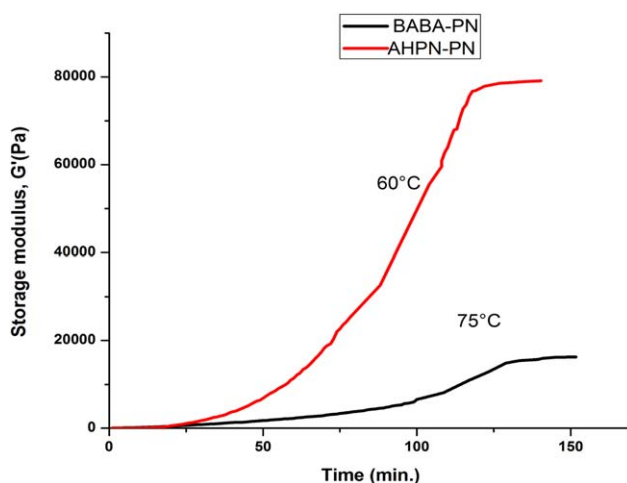


Figure 7. Variation in storage modulus with time for BABA-PN and AHPN-PN (uncatalyzed), heating rate 5°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

After curing at 120°C for 16 h, the azide and propargyl groups disappeared and new peaks appeared at $1370\text{--}1390$ and $1470\text{--}1490\text{ cm}^{-1}$ because of $\text{N}=\text{N}$ in triazole rings as evident in Figure 4. Scheme 3 depicts the reaction of azide and propargyl functions.

The cure reactions of AHPN-PN were studied by DSC using a 1 : 1 (molar) blend of azide and propargyl groups. The nonisothermal DSC showed two exotherms for both catalyzed and uncatalyzed cases as shown in Figure 4. The first exotherm is attributed to the click cure reaction. Since complete reaction of all the azide groups cannot take place during the dynamic ramping of temperature, the residual azide groups decompose at higher temperature. This is manifested as a second exotherm at around 200°C. Such a phenomenon has already been reported in a previous work.³¹ The origin of the second exotherm in DSC in both catalyzed and uncatalyzed DSC thermogram was investigated. On catalysis, the first exotherm gets shifted to lower temperatures considerably, while the second

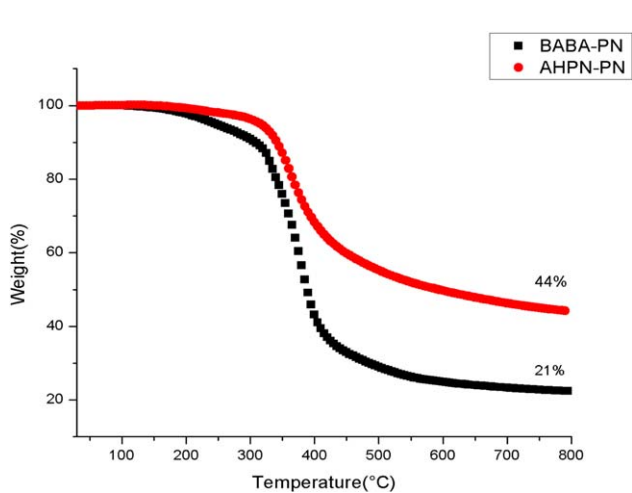


Figure 8. Thermograms of BABA-PN and AHPN-PN cured blends (1 : 1, catalyzed). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

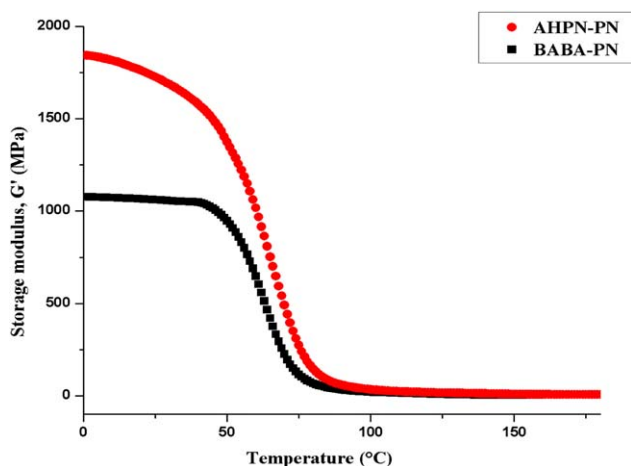


Figure 9. Variation of storage modulus with temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shifts only marginally. DSC of the azide containing monomer AHPN showed an exotherm [Figure 5(a)] at the same temperature as the second exotherm in the mix (Figure 4). Moreover, TGA of the azide monomer showed a mass loss at the same temperature range [Figure 5(b)]. The mass loss at this stage was estimated as 20%. It is assumed that azide group loses one nitrogen molecule on decomposition. The mass loss is 15% while a loss of azide group as a whole would result in 22% mass loss. Considering the mass loss from the phenolic backbone, the mass loss observed in TGA of AHPN at around 200°C can be assigned to the decomposition of the unreacted azide group.

Accordingly, the apparent enthalpy of curing was computed to be 172 kJ/mol for the catalyzed click cure reaction. Earlier studies reported 231 kJ/mole for catalyzed system.³¹ As the mix is subjected to a rapid temperature scan, the system does not get enough time to undergo complete click reaction. As a consequence, the residual azide groups decompose at nearly 200°C. On catalysis, the proportion of click cure reaction increases and thus the second exotherm becomes less predominant in this

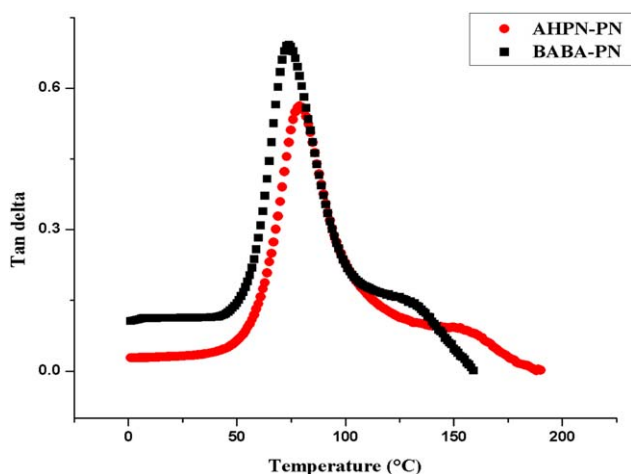


Figure 10. Variation of tan delta with temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

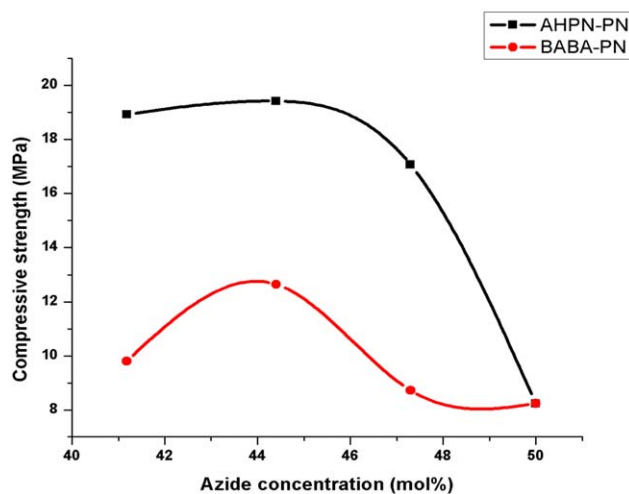


Figure 11. Comparison of compressive strength of foam composites from AHPN-PN and BABA-PN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

case. The amount of unreacted azide was calculated from the residual exotherm as 13%. The heat of decomposition of AHPN was estimated as 184 kJ/mol. The residual heat of decomposition is 25 and 102 kJ/mol (based on the concentration of AHPN alone originally added in the mix) for the catalyzed and uncatalyzed systems. This led to the calculation of the unreacted AHPN as 13 and 56 mol %, respectively, in the catalyzed and uncatalyzed systems, respectively. Thus, the corrected heat of cure reaction is 198 kJ/mol.

Rheological Studies

Rheological experiments were performed for BABA-PN and AHPN-PN systems under dynamic heating condition (30–200°C) and at different isothermal (60°C and 75°C) conditions as shown in Figures 6 and 7, respectively. Cure is initiated at nearly the same temperature range as seen in DSC. AHPN leads

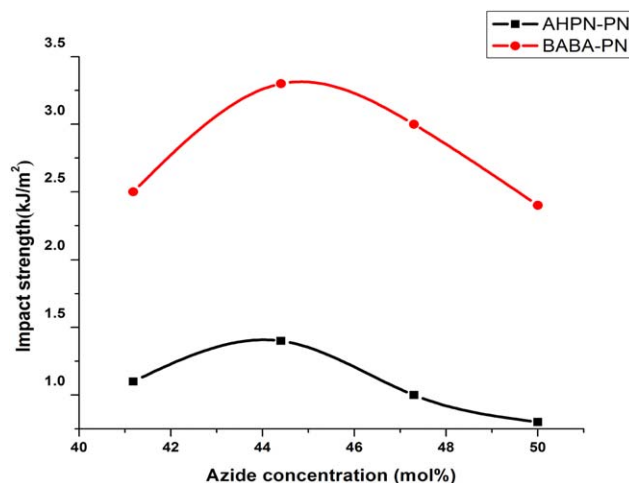


Figure 12. Comparison of impact strength of foam composites from AHPN-PN and BABA-PN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

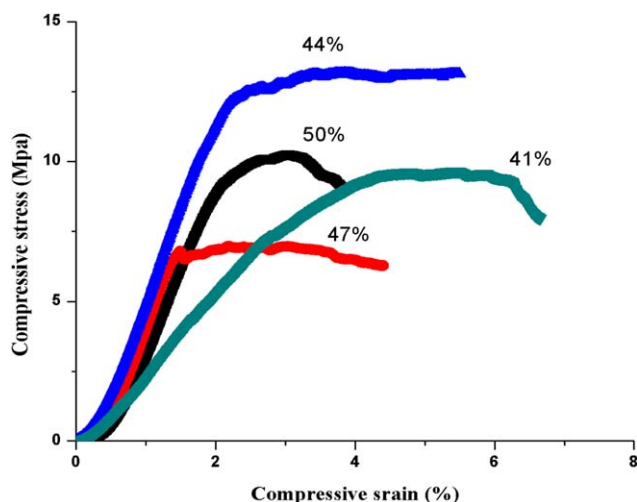


Figure 13. Stress–strain graph of syntactic foams of BABA-PN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to higher modulus because of its multifunctional character (more cross-linking).

Isothermal rheological studies further confirmed the higher cross-linking characteristics of AHPN. While the cure stagnated in about 135 min at 60°C for AHPN, BABA needs a higher thermal activation (75°C) for attaining the cure stagnation during this time.

Thermo gravimetric Analysis of Cured Resins

Thermal decomposition behavior of the completely cured BABA-PN and AHPN-PN blends was investigated by thermo gravimetric analysis (Figure 8). Major mass loss of the networks was observed at 350°C because of the decomposition of triazole and novolac backbone. The AHPN system showed an improved thermal stability because of the increased aromatic content and cross-linking. Char residue at 800°C for the

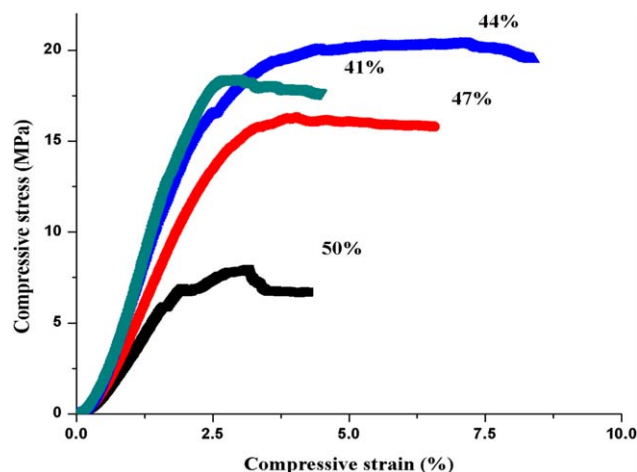


Figure 14. Stress–strain graph of syntactic foams of AHPN-PN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

AHPN-PN system was found to be 44% against 21% for the BABA-PN system.

Dynamic Mechanical Studies

The DMA of the cured BABA-PN and AHPN-PN resins featured glass transition temperatures of 73°C and 78°C, respectively. The storage modulus was greater than 1 GPa (Figures 9 and 10). It is evident from DMA spectra that the glass transition temperature and storage modulus were higher for the AHPN system because of increased cross-link density and rigidity of the polymer backbones, as expected.

Mechanical Properties of Syntactic Foams

Syntactic foam composites of density 0.55 g/cc were processed using click resins and glass microballoon along with silica fiber reinforcement, in the weight ratio of 100 : 80 : 30. Microballoon k 25 and k 37 were mixed in equal quantities to constitute 80 phr. Thickness and volume of the composite were controlled so as to achieve the required density of 0.55 g/cc. The mechanical properties of syntactic foams generally depend on density of the foam, which in turn depends on resin–reinforcement–filler ratio.³² Compressive strength decreased with increasing cross-link density (maximum at 44 mol % azide concentration) and the trend is more prominent in the case of AHPN-PN system because of the more rigid and highly packed phenolic network structures in this case as in Figure 11. This can lead to embrittlement of the matrix as a whole. At higher proportions of propargyl functions in AHPN-PN blend, cross-link densities are lower and flexibility is imparted by the unreacted propargyl groups. This is supported by the corresponding values of impact strengths as seen in Figure 12.

It is evident that both compressive and impact strength level off at 44 mol % of azide (with respect to propargyl groups) at which, there is an effective balancing of embrittlement and flexibilization. The behavior of the foam composites during compressive loading is shown typically in Figures 13 and 14. It is seen that the area under the stress–strain curves is maximum for 44 mol % of azide concentration in both the systems, implying better toughness for this composition. Stoichiometric imbalance is conducive for generating tougher matrix by way of reducing cross-link density. Mechanical properties of resole-phenolic resin based syntactic foam of comparable density showed a compressive strength of 12–15 MPa.²⁷ This is comparable to those of present system. However, their impact strength is inferior (0.94 kJ/m²). However, in contrast to the resole, the present system is curable by addition reaction at a relatively low temperature (resole needs curing at > 150°C)

Morphological Evaluation of Syntactic Foams

The SEM picture reveals a brittle fracture for the matrix with 50 mol % composition for both AHPN and BABA. Decreasing the relative proportion of azide component ensured better filler wetting and consequently improved mechanical properties of the resultant syntactic foam composites. The toughened nature of the composite is clearly seen by the better wetting of the microballoon and the silica fiber in the SEM images (Figure 15) of syntactic foams with 44 mol % azide. On the other hand, in the case of 50 mol % azide concentration, both the resin

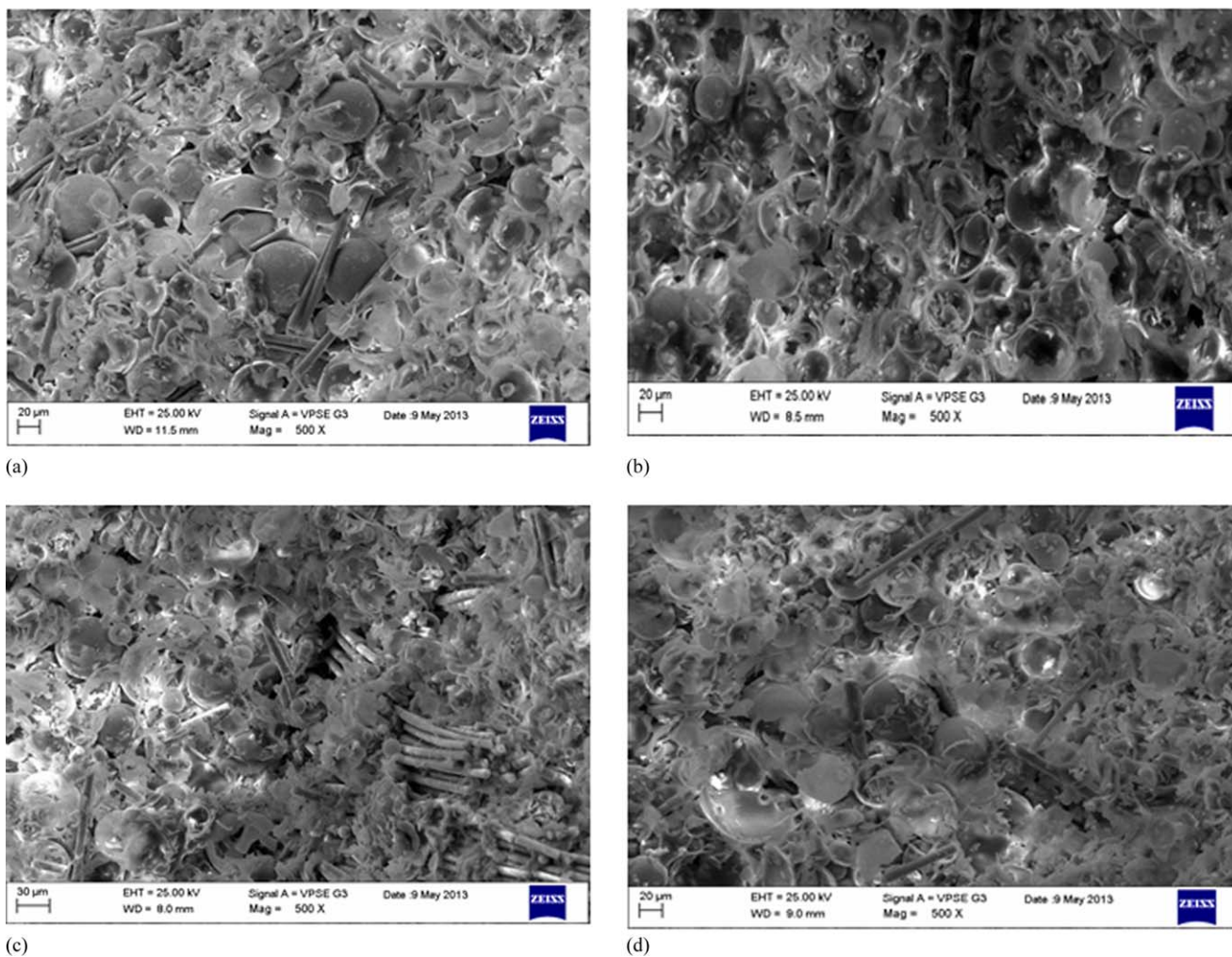


Figure 15. SEM images of the syntactic foam composites with different azide concentrations. (a) 50 mol % AHPN, (b) 44 mol % AHPN, (c) 50 mol % BABA, and (d) 44 mol % BABA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

systems show fiber pull out and improper fiber wetting as manifested in their impact strength.

CONCLUSIONS

A low temperature addition curable phenolic-epoxy resin system was derived by anchoring clickable groups to epoxy and novolac resins that enabled them to undergo curing by click reaction. Azide group was attached to epoxy resin and propargyl groups on to novolac resin. This new phenolic-epoxy network contained triazole cross-links. The cure reaction was catalyzed by Cu_2I_2 . The cured resin showed T_g in the range of 73–78°C. Thermal stability, T_g and modulus increased for the propargyl novolac cured by the polyazide (AHPN) rather the diazide (BABA). The impact properties of the syntactic foam derived from the resin were better for the diazide based network because of reduced cross-linking. The compressive strength of the foams showed an increasing trend when the azide stoichiometry is shifted away from 1 : 1 equivalent. The properties optimized at 44 mol % azide concentration. This click reaction has been successfully extrapolated to derive low temperature curable epoxy-phenolic resins. These phenolic-epoxy systems

appear to be better resins than the conventional phenolic-epoxy resin system in terms of their addition curing nature at low temperature.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Director, VSSC for granting permission to publish this work. They also thank the Analytical and Spectroscopy Division and Material Characterisation Division of VSSC for the analytical support.

REFERENCES

- Mingcun, W.; Liuhe, W.; Tong Z. *Polymer* **2005**, *46*, 9202.
- Brydson, J. A. *Plastic Materials*, 7th ed.; Butterworth Heinemann: Oxford, **1999**.
- Kopf, P. W.; Little, D. *Phenolic resins*, 3rd ed. In *Encyclopedia of Chemical Technology*; Grayson, M.; Kirk-Othmer, E. D., Eds.; Wiley: New York, **1991**; Vol. 18, p 603.
- Shinn-Shyong, T.; Ya-Ga, C. *Mater. Chem. Phys.* **2002**, *73*, 162.

5. Sandler, S. R.; Karo, W. *Polymer Syntheses*, 2nd ed.; Academic Press: Boston, **1992**, Vol. 1, Chapter 1.
6. Kazuhisa, H.; Masakatsu, A. *React. Funct. Polym.* **2013**, *73*, 256.
7. Sturiale, A.; Vazquez, A.; Cisilino, A.; Manfredi, L. B. *Int. J. Adhes. Adhes.* **2007**, *27*, 156.
8. Reghunadhan Nair, C. P. *Prog. Polym. Sci.* **2004**, *29*, 401.
9. Ambika Devi, K.; Bibin, J.; Reghunadhan Nair, C. P.; Ninan, K. N. *J. Appl. Polym. Sci.* **2007**, *105*, 3715.
10. David, D. D.; Sreenivas, P.; Philipp, H.; Andrew, K. M.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G. *J. Polym. Sci. Polym. Chem.* **2004**, *42*, 4392.
11. Wolfgang, H. B.; Sachsenhofer, R. *Macromol. Rapid Commun.* **2007**, *28*, 15.
12. Opsteen, J. A.; Jan, C. M.; van ,H. *J. Polym. Sci. Polym. Chem.* **2007**, *45*, 2913.
13. Mansfeld, U.; Pietsch, C.; Hoogenboom, R.; Remzi, B.; Schubert, U. S. **2010**, *Polym. Chem. 1*, 1560.
14. Stacy, S.; James, B.; Haddleton, D. M.; Remzi, B. C. *Eur. Polym. J.* **2011**, *47*, 435.
15. Dohler, D.; Michael, P.; Binder, W. H. *Macromolecules* **2012**, *45*, 3335.
16. Tsarevsky, N. V.; Sumerlin, B. S.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 3558.
17. Gao, H.; Louche, G.; Sumerlin, B. S.; Jahed, N.; Golas, P.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 8979.
18. Opsteen, J. A.; van , H.; Jan, C. M. *Chem. Commun.* **2005**, *1*, 57.
19. Parrish, B.; Breitenkamp, R. B.; Emrick, T. J. *Am. Chem. Soc.* **2005**, *127*, 7404.
20. Dag, A.; Durmaz, H.; Demir, E.; Hizal, G.; Tunca, U. *J. Polym. Sci. Polym. Chem.* **2008**, *46*, 6969.
21. Durmaz, H.; Dag, A.; Hizal, A.; Hizal, G.; Tunca, U. *J. Polym. Sci. Polym. Chem.* **2008**, *46*, 7091.
22. Nagai, A.; Kamei, Y.; Wang, X. S.; Omura, M.; Sudo, A.; Nishida, H.; Kawamoto, E.; Endo, T. *J. Polym. Sci. Polym. Chem.* **2008**, *46*, 2316.
23. Sunitha, K.; Santhosh Kumar, K. S.; Dona, M.; Reghunadhan Nair, C. P. *Mater. Lett.* **2013**, *99*, 101.
24. Bindu, R. L.; Reghunadhan Nair, C. P.; Ninan, K. N. *Polym. Int.* **2001**, *50*, 651.
25. Bibin, J.; Dona, M.; Deependran, B.; George, J.; Reghunadhan Nair, C. P.; Ninan, K. N. *J. Mater. Sci.* **2011**, *46*, 5017.
26. Bipin, J.; Reghunadhan Nair, C. P.; Ninan, K. N. *Cell. Polym.* **2007**, *26*, 229.
27. Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Edit.* **2001**, *40*, 2004.
28. Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057.
29. Tsarevsky, N. V.; Bernaerts, K. V.; Dufour, B.; Du Prez, F. E.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 9308.
30. Lutz, J. F.; Börner, H. G.; Weichenhan, K. *Macromol. Rapid Commun.* **2005**, *26*, 514.
31. Smitha, C. S.; Sunitha, K.; Dona, M.; Reghunadhan Nair, C. P. *J. Appl. Polym. Sci.* **2013**, *130*, 1289.
32. Bipin, J.; Reghunadhan Nair, C. P. Update on syntactic foams. *Ismiters rapra UK*, **2010**.