Indian Journal of
Advances in Chemical Science

Review Article

Self-Healing Epoxy Composites: A Review

Aransha Maurya*, Nanda Tiwari, Sonika Bhatia*

Department of Chemistry, Isabella Thoburn College, Lucknow, Uttar Pradesh, India

ABSTRACT

This article reviews both intrinsic and extrinsic epoxy composites and their self-healing mechanisms. Epoxy resin composites are polymeric epoxide composite materials capable of automatic repair when damaged, thus have become very popular in recent years. With time, small damage and micro-cracks in epoxy composites are very common so requires regular inspection and maintenance. The self-healing concept minimizes repair costs and increases the lifespan of the material. The addition of functional composite material such as hollow fiber and microcapsules helps to repair the cracks of epoxy materials in extrinsic self-healing composites. Whereas, the intrinsic self-healing mechanism is based on physical and chemical interactions. Epoxy composites due to their exceptional strength, chemical, and heat resistance have superb load-bearing properties, therefore, find wide applications in aerospace, automotive, and construction industries.

Key words: Aerospace, Epoxy composites, Hollow fiber, Microcapsule, Self-healing.

1. INTRODUCTION

Epoxy resins are polymers of epoxides [1]. Epoxides, also referred as oxiranes, are highly strained three-membered rings that easily open and undergo copolymerization crosslinking with themselves in the presence of a catalyst or with other compounds containing active hydrogen-like amines, phenols, thiols, etc., to yield thermosetting polymers [2]. The cross-linking reaction is referred to as curing while the co-reactants are referred to as curatives or hardeners [3]. These resins have low shrink during cure and possess well electrical and insulating properties, tough mechanical properties, and excellent moisture and chemical resistance. Thus, the epoxy resin can be used for a variety of applications in home appliances, transportation (automobile, aircraft, spacecraft, and ships), civil engineering, electronic technology and sporting goods [4]. But these, thermosetting epoxy resin-based materials can undergo wear and tear that is carbon fiber-reinforced when exposed to mechanical, chemical, thermal, and ultraviolet radiation leading to local damage and micro-cracks generation [5]. Due to its wide range of applications, there is a prime need to extend the service life of polymers and avoid micro-cracks. Since the last decade, epoxy self-healing composites have been developed which self-heal the developed micro-crack much like the lizard regrows her chopped tail and our bruised skin self-heals [6].

2. EXTRINSIC SELF-HEALING

The extrinsic self-healing mechanism is based on the use of a healing agent placed in the matrix [7]. The two main extrinsic self-healing approaches are explained below:

2.1. Hollow Fiber Embedment

Inspired by the natural phenomenon of self-healing, many types of research have been done on the hollow fiber method to overcome the micro-damage that occurs in the epoxy polymer in the form of fatigue and impact through the external force [8]. When the epoxy polymer receives any external impact or fatigue, the hollow fiber breaks and releases a repairing or healing liquid into the cracks to fill the damage as shown in Figure 1. The hollow fibers filled with healing liquid are embedded into the matrix as carbon fiber-reinforced plastic composites, or glass fiber-reinforced plastic, through a vacuum-assisted resin transfer molding process [9]. By the means of co-electrospinning, ultrathin self-healing fibers are fabricated. In this method, dicyclopentadiene (DCPD) works as a healing agent wrapped into polyacrylonitrile (PAN) to form core-shell nanofibers. To transport the healing agent to longer distances and enhance the efficiency of the healing agent the 3D microvascular method is adopted in which a vascular network is developed in the matrix to store the healing agent [10].

2.2. Microcapsule Method

Capsule-based self-healing composite was first created by White *et al*. [12] in 2001. In this method, small cell-like capsules containing DCPD and Grubb's catalyst (it is transition metal carbene complexes) present in the polymer matrix are taken. Due to crack formation in composites, capsules are ruptured and the released healing agent DCPD comes in contact with Grubb's catalyst, then ring-opening metathesis polymerization (ROMP) is triggered which heals the crack planes as shown in Figure 2. ROMP is a chain-growth polymerization process where a mixture of cyclic olefin is converted to a polymeric material. ROMP reaction shows rapid polymerization at ambient conditions, high stability, low monomer viscosity, and volatility.

Two-component healing agents – epoxy and mercaptan were incorporated in poly (methyl methacrylate) PMMA shells. The self-healing mechanism of epoxy composites and the effect of the healing agent on mechanical properties were investigated. The tensile strength

***Corresponding author:**
E-mail: aranshamaurya@gmail.com; sonikaitc2@gmail.com

ISSN NO: 2320-0898 (p); 2320-0928 (e)
DOI: ***

Received: 08th October 2021;
Revised: 22nd October 2021;
Accepted: 23rd October 2021

of the composite increased initially with 2.5wt% PMMA microcapsule and then decreased gradually with increasing microcapsule content up to 10%PMMA microcapsule. After 24 h, at room temperature, 80% healing efficiency was achieved with a 10 wt% PMMA microcapsule, and fracture toughness of the composites was measured [13].

3. INTRINSIC SELF-HEALING

Intrinsic self-healing is based on specific properties of composites such as molecular structures, physical and chemical bonds, and the performance of the polymers which heals the crack. It often requires external stimuli such as high temperature. It can be classified into physical and chemical interactions.

3.1. Physical Interactions

The interdiffusion and entanglement of polymer chains are the elementary step of all physical self-healing mechanisms. Both the properties depend on intermolecular forces. Self-healing of cracks involves a 5-stage mechanism proposed by Wool and O'Connor [14] to define the complex strength recovery process of ruptured polymer/polymer interfaces. The following steps are: (a) Surface rearrangement, (b) surface approach, (c) wetting stage, (d) diffusion, and (e) randomization stage. Based on physical interactions, there are two types of polymer blends:

3.1.1. Miscible polymer blends

The addition of thermoplastic modifiers is another self-healing technique for epoxy resin. Hayes *et al*. [15] demonstrated thermally activated epoxy composite using thermoplastic modifiers with linear copolymer (polybisphenol-A-co-epichlorohydrin) can heal the cracks by short-distance diffusion of molecular chains. Thermoplastic is required to be miscible within the epoxy resin. Increasing the healing temperature and amount of thermoplastic agent increases healing efficiency. 20 wt% of healing agents present in epoxy composites when healed at 140°C led to 64% recovery of impact strength. Luo *et al*. [16] demonstrated an epoxy/polycaprolactone (PCL) phase-separated blend. About 15.5% of PCL composed of initially miscible blend during cross-linking of the epoxy, it undergoes polymerization induced phase separation producing bricks and mortar morphology where epoxy spheres (bricks) are interconnected with PCL matrix (mortar). It became fully cured and strong. On cooling, recrystallization of PCL leads to crack closure.

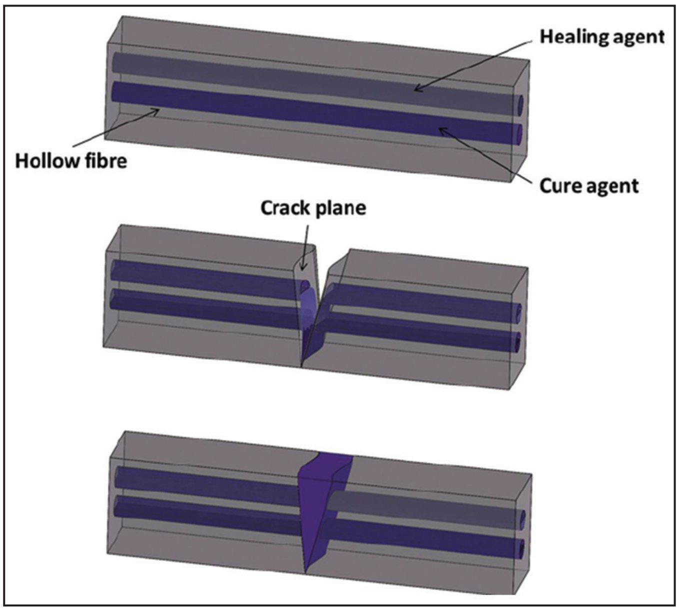

Figure 1: Hollow fiber based self-healing mechanism [11].

3.1.2. Immiscible polymer blends

Meure *et al*. [17] used a thermoplastic healing agent that is poly (ethylene -co- methacrylic acid) (EMMA) and found that it can be effective for both epoxy polymer and carbon fiber epoxy composites. EMMA is immiscible and disperses as particles or fine fibers within the epoxy resin. A condensation reaction between acid functional groups in the EMMA and residual hydroxyl groups in the cured epoxy matrix develops a pressure delivery mechanism, catalyzed by tertiary amine groups it produces water which forms high-pressure micron-sized bubbles within the EMMA that swell the thermoplastic and the high internal pressure forces the EMMA, which is molten at elevated temperature into open cracks and repair damage.

3.2. Chemical Interactions

3.2.1. Thermo Reversible Reaction (Diels-Alder [DA] and Retro-DA Reactions)

DA reaction is a well-known reversible cross-linking reaction studied for intrinsic self-healing materials. DA adducts are mainly used for self-healing processes as they are less expensive and easily available commercially [18]. Chen *et al*. [19] have used furan-maleimide monomer system to synthesize thermally reversible highly cross-linked polymeric materials through DA reaction as shown in Figure 3.

Peterson *et al*. [20] have shown that after the occurrence of damage, when the system was mended with epoxy-amine thermoset as a healing gel, the efficiency of the system was found to be low (37%) which has been improved up to 70% by adding DMF dissolved bismaleimide (BMI), here furan groups were used in the synthesis of epoxy backbone. However, this method has its drawbacks and limitations due to its long healing time, use of solvents, and encapsulated reagents. Diamine DA adduct was synthesized by Kuang *et al*. [21] as a curing agent for epoxy resin in which repeated self-healing and rapid recovery were analyzed through nuclear magnetic resonance, Fourier transform

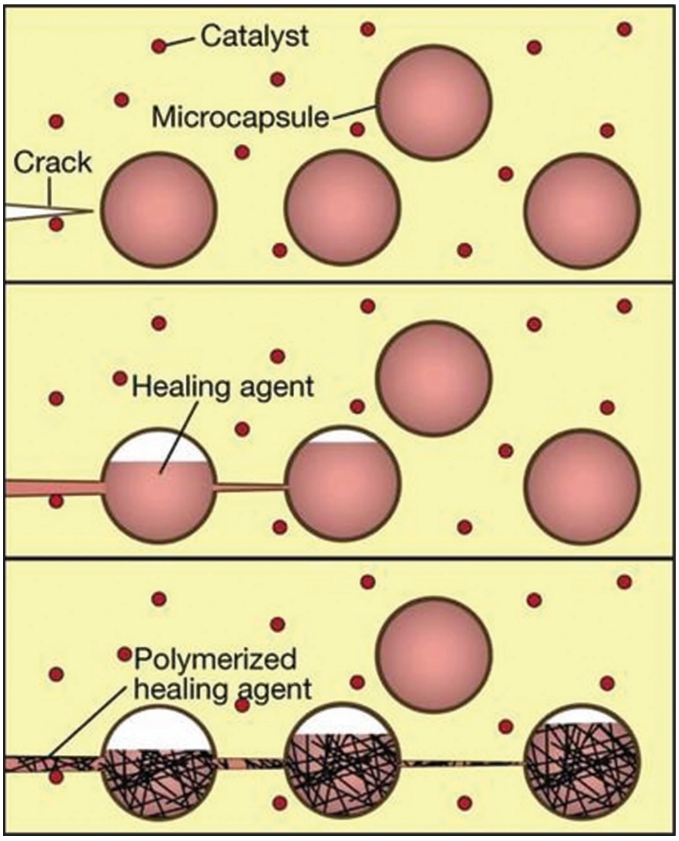

Figure 2: Microcapsule based self-healing mechanism [12].

infrared, and differential scanning calorimetry in a thermal cyclic test. Although many successful self-healing methods are reported on DA adducts, it is also evident that they have poor mechanical and thermal properties when multiple healing cycles are examined. To overcome these disadvantages, Peterson *et al*. [22] introduced DA adducts into the interphase of glass fiber-reinforced composites in which furan groups are embedded within epoxy matrices. To swell the network structure in epoxy resins he diffused self-healing agents loaded with DMF and N, N'-(4, 4′-methylene diphenyl) BMI onto furan-functionalized epoxy resins. This swell-up network forms the contact between the cracked surfaces which enables thermal reversible reaction between furan and maleic anhydride (Figure 4) that results in repairment of crack.

Yet the kinetics of self-healing is slow and even slower for high molecular weight polymers. To resolve this issue, a recyclable high-performance and fast self-recovering cross-linked epoxy resin/graphene nanocomposite was designed by Cai *et al*., [24]; these graphenes provide self-healing not only through heat but also through microwaves and IR. Recently a novel, flexible self-healing epoxy material was fabricated with graphite nanosheet (GNSs) by Guo *et al*. [25]. Lap shear strength has proven that GNSs have more than 90% self-healing efficiency. In 2019, Khan *et al*. [26] have designed thermo-reversible self-healing nanocomposites by hybridizing graphene nanoplatelet in a polymer matrix with thermo- irreversible diglycidyl ether of bisphenol A (DGEBA) epoxy resin. The healing behavior is good over five cycles of repeated self-healing although the healing efficiency is below than 100%. There is still a need for more advanced research for easier and faster epoxy material processing techniques.

3.2.2. Transesterification reaction

Capelot *et al*. [27]. reported that without altering the degree of cross-linking a resin material can change its overall cross-linking structure through an interesterification reaction. They showed that at high temperature the material can be processed repeatedly as it behaves as a thermoplastic while at low temperature it forms thermosetting epoxy polymers due to freezing of molecular chains formed by transesterification. Therefore, epoxy polymers based on ester exchange reactions are considered ideal for recycling. Ding *et al*. [28] described a novel high-performance thermosetting epoxy polymer/chain-extended BMI (EP/CBMI) system with dynamic transesterification bonds, yielding relatively high glass transition temperature polymers which have high recovering properties to its original shape within 21s at 250°C, whereas their healing efficiency is 78–87% up to the second cycle of healing. Lu and Li [29] study focused on the recyclability property and designed a DGEBA-phthalic anhydride system which has a healing efficiency of 88%. This test showed that recycling not only depends on pressure and temperature but also on particle size and milling time.

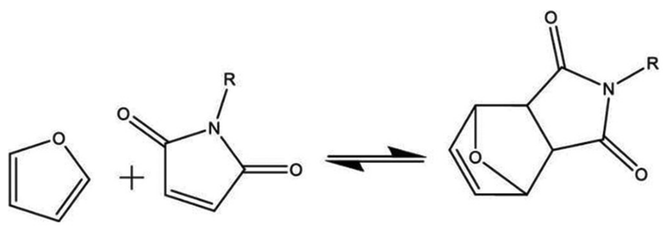

Figure 3: DA/rDA reaction between a furan group and maleimide group [18].

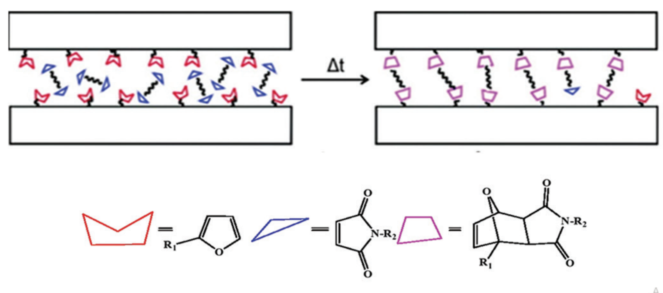

Figure 4: On the nanometer scale, the furans along the crack surfaces react with BMIs across the crack surface [23].

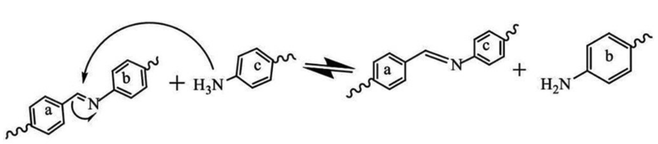

Figure 5: Imine exchange dynamic reaction [30].

3.2.3. Imine exchange dynamic reaction

Imine bond is considered best for healing epoxy vitrimers as imine can react in three ways simultaneously including imine metathesis, imine exchange (Figure 5), and imine hydrolysis or condensation and there is no need for catalyst, heat, monomers, and pressure.

By the condensation of lignin-derived vanillin and methylcyclohexane diamine Memom *et al*. [31] synthesized imine-based epoxy hardener. On curing, epoxy resin with this hardener provides good tensile strength and makes a solvent resistance system.

4. SELF-HEALING COMPOSITES IN AEROSPACE APPLICATIONS

Self-healing composites are extensively used in the field of aerospace. Self-healing ceramic composites are used in jet engines. Boron and boron silicon glass are present in ceramics, when these are oxidized then self-healing is achieved and this seals the cracks. To overcome the poor impact resistance of fiber-reinforced plastic, self-healing carbon fiber-reinforced epoxy was synthesized by Bond *et al*. [32]. Super elastic shape memory Ni-Ti alloys wires are used in composites with carbon fabrics or glass fabrics which improve the impact properties [32]. Self-healing for an aerospace-grade E glass (electrical grade glass) epoxy plate by incorporating a series of vascular networks was demonstrated by Coope *et al*. [33] here self-healing agent was Lewis acid-catalyzed epoxy. Hence, it has good mechanical strength and can be an effective substitute for aerospace fiber reinforced polymer composites. Self-healing composites are also used in several other structural applications.

5. CONCLUSION

Epoxies have excellent mechanical strength, great thermal stability, resistance to corrosion, and good adhesion to substrates. Today self-healing epoxy composites can be considered as a new class of material and have great significance. The self-healing mechanism increases the lifespan of composites by repairing the cracks and damages. In this review, several examples of both extrinsic and intrinsic self-healing epoxy materials have been cited and their repair mechanism explained.

6. ACKNOWLEDGMENT

The authors acknowledge to Dr. (Mrs.) V. Prakash, The Principal, Isabella Thoburn College, Lucknow, for the support.

7. REFERENCES

1. Available from: http://www.corrosionpedia.com/1746/epoxy-resin [Last accessed on 2021 Oct 05].
2. P. G. Gibson, (2017) Brydson's plastic material, ***Science Direct***,

8: 773-797.
3. Available from: https://dianhydrides.com/what-epoxy-composites [Last accessed on 2021 Oct 05].
4. J. C. Capricho, B. Fox, N. Hameed, (2019) Multifunctionality in epoxy resins, ***Polymer Reviews***, **60:** 2-5.
5. M. N. D. Santos, C. V. Opelt, S. H. Pezzin, L. A. F. Coelho, (2013) A review on photo-curing of epoxy resins, ***International Journal of Technical Research and Science***, **16:** 367.
6. M. J. Harrington, O. Speck, T. Speck, S. Wagner, (2015) *Biological Archetypes for Self-Healing Materials*, Vol. 273. Berlin: Springer International Publishing, p307-344.
7. *Extrinsic Self-Healing Polymers*, (2021) Available from: Available from: https://polymerdatabase.com/polymer%20chemistry/self-healing%20Polymers.html [Last accessed on 2021 Oct 06].
8. Z. Fenglei, M. Yaseen, K. Huang, (2020) A review on the self-healing ability of epoxy polymers, ***Applied Polymer Science***, **138:** 2-4.
9. C. Dry, N. Sottos, (1993) Passive smart self-repair in polymer matrix composite, ***Conference of Adaptive Materials***, **1916:** 438-444.
10. T. D. Nath, J. K. Banshiwal, (2018), ***Self-Healing Polymer Composites for Structural Application***, Available from: http://intechopen.com/chapter/64985 [Last accessed on 2019 Dec 23].
11. M. D. Banea, R. Campilho, C. Sato, (2014) ***Smart Adhesive Joints: An Overview of Recent Developments***, Available from: http://researchgate.net/figure [Last accessed on 2021 Oct 06].
12. S. R. White, N. R. Scottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, E. N. Brown, S. Viswanathan, (2001) Autonomic healing of polymer composites, ***Nature***, **409:** 794-797.
13. F. Ahangaran, M. Hayaty, A. H. Navarchian, Y. Pei, P. Francesco, (2019) Development of self-healing epoxy composites via incorporation of microencapsulated epoxy and mercaptan in poly (methyl methacrylate) shell, ***Polymer Testing***, **73:** 395-403.
14. R. P. Wool, K. M. O'Connor, (1981) A theory of crack healing in polymers, ***Journal Applied Physics***, **52:** 5953-5963.
15. S. A. Hayes, F. R. Jones, K. Marsiya, W. Zhang, (2007) A self-healing thermosetting composite material, ***Composites Part A: Applied Science and Manufacturing***, **38:** 1116.
16. X. Luo, R. Ou, D. E. Eberly, A. Singhal, W. Viratyaporn, P. T Mather, (2009) A thermoplastic/thermoset blend exhibiting thermal mending and reversible adhesion, ***ACS Applied Materials and Interfaces***, 1: 612-620.
17. S. Meure, D. Y. Wu, S. Furman, (2009) Polyethylene-co-methacrylic acid healing agent for mendable epoxy resins, ***Acta Materialia***, **57:** 4312-4320.
18. R. K. Bose, M. H. Santana, P. Stefano, (2021) Intrinsic self-healing epoxies in polymer matrix composites (PMCs) for aerospace applications, ***Polymers***, **13:** 11-13.
19. X Chen, M. A. Dam, K. Sheran, F. Wudl, (2000) A thermally re-mendable cross-linked polymeric material, ***Science***, **295:** 1698-1702.
20. A. M. Peterson, R. E. Jensen, G. R. Palmese, (2009) Reversibly cross-linked polymer gels as healing agents for epoxy-amine thermosets, ***ACS Applied Materials and Interfaces***, **1:** 992-995.
21. X. Kuang, X. Dong, D. Wang, (2015) Facile fabrication of fast recyclable and multiple self-healing epoxy materials through diels-alder adduct cross-linker, ***Journal of Polymer Science Part A Polymer Chemistry***, **53:** 2094.
22. A. M. Peterson, R. E. Jensen, G. R. Palmese, (2011) Thermoreversible and remendable glass-polymer interface for fiber-reinforced composites, ***Composite Science Technology***, **71:** 586-592.
23. A. M. Peterson, R. E. Jensen, G. R. Palmese, (2010) Room-temperature healing of a thermosetting polymer network using the diels-alder reaction, ***ACS Applied Materials and Interfaces***, **2:** 2169.
24. A. Cai, Y. Zhang, X. Zou, R. Zhang, X. Wang, P. Sun, (2017) Rapid self-healing and recycling of multiple-responsive mechanically enhanced epoxy resin/graphene nanocomposites, ***RSC Advances***, **7:** 46336-46343.
25. Y. Guo, D. Zou, D. X. Yang, P. Zhao, C. Chen, M. Shuai, (2019) Infrared induced repeatable self-healing and removability of mechanically enhanced graphene-epoxy flexible materials, ***RSC Advances***, **9:** 14024-14032.
26. N. I. Khan, S. Halder, J. Wang, (2019) Diels-alder based epoxy matrix and interfacial healing of bismaleimide grafted GNP-infused hybrid nanocomposites, ***Polymers***, **74:** 138-151.
27. M. Capelot, D. Montarnal, L. Leibler, (2012) Metal-catalyzed transesterification for healing and assembling of thermosets, ***Journal of the American Chemical Society***, **134:** 7664.
28. Z. Ding, L. Yuan, Q. Guan, G. Liang, (2018) A reconfiguring and self-healing thermoset epoxy/chain-extended bismaleimide resin system with thermally dynamic covalent bonds, ***Polymer***, **147:** 170-182.
29. L. Lu, G. Li, (2016) Intrinsic healable and recyclable thermoset epoxy based on shape memory effect and transesterification reaction, ***Polymer***, **105:** 10-18.
30. Z. O. Lei, P. Xie, M. Q. Zhang, (2015) Catalyst-free dynamic exchange of aromatic schiff base bonds and its application to self-healing and remolding of crosslinked polymers, ***Journals of Material Chemistry A***, **3:** 19662.
31. H. Memom, Y. Wei, W. Liu, Q. Jiang, L. Zhang, (2020) An imine-containing epoxy vitrimer with versatile recyclability and its application in fully recyclable carbon fiber reinforced composites, ***Composites Science and Technology***, **199:** 108314.
32. I. P. Bond, R. S.Trask, H. R. Williams, (2008) Self-healing fiber-reinforced polymer composites, ***MRS Bulletin***, **33:** 770-774.
33. T. S. Coope, D. F. Wass, R. S. Trask, I. P. Bond, (2014) Metal triflates as catalytic curing agents in self-healing fibre reinforced polymer composite materials, ***Macromolecular Materials and Engineering***, **299:** 208-218.

Bibliographical Sketch

Ms. Aransha Maurya pursuing a master's in chemistry from Isabella Thoburn College, Lucknow and recently completed a one-month internship at Duromax Hitech Coatings.

Ms. Nanda Tiwari pursuing a master's in chemistry from Isabella Thoburn College, Lucknow and recently completed a one-month internship at Duromax Hitech Coatings.

Dr (Mrs) Sonika Bhatia, Associate professor, Department of chemistry, Isabella Thoburn College, Lucknow. She received her PhD from Central Drug research Institute, Lucknow & has done post-doctoral research from department of chemistry IIT Kanpur. She has 8 papers, 3 book chapters & 1 patent to her credit. Dr. Bhatia has been awarded first place in the Broad Outlook learner Teacher award by Air India at the state level.