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Functional enhancement of epoxy polymer nanocomposite: A nano blended binder for retrofitting of bridges

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ABSTRACT
Fiber reinforced polymer (FRP) composites are playing a vital role in repair and rehabilitation application, due to their inherent tensile properties. Epoxy polymers are used as bonding agent in the FRP applications. As epoxy is moisture sensitive, it is very much required to tailor them to make it hydrophobic to control the delamination of epoxy at interface. In the present study, functional modification of epoxy by using nano SiO_2 has been conducted. Micro-analytical characterization techniques have been conducted to study the interaction of nano SiO_2 with epoxy resin. It is found that matrix toughening has increased due to nano modification leading to increased hydrophobicity. Based on the experimental findings, it is concluded that the nano blended epoxy resin for FRP composites can be an effective repair binder for retrofitting of berdges.
Keywords: *FRP, Epoxy, Polymer nanocomposites, Retrofit*

1. Introduction

Fiber reinforced polymers or plastics (FRP) is one of the most important repair and rehabilitation material in civil/structural engineering mainly for the structures that are built in coastal/marine environment, as severe damages occur due to salt exposure. Application of advanced composite materials are mainly used for (i) rehabilitation, including the applications towards repair, strengthening and retrofit of structures; and (ii) new construction with all Fiber reinforced Polymers solutions or new composite FRP/concrete systems. The FRP wrapped or retrofitted bridge columns are shown in Fig 1. The widely used FRPs are Carbon Fiber Reinforced Polymer (CFRP) and Glass Fiber Reinforced Polymers (GFRP), each of them have their own advantages and disadvantages based on the engineering need. When compared to mild steel strength, FRP composites exhibit a typical stress–strain response as a linear elastic stress–strain behavior before brittle failure by rupture. Hence, this behavior proved the important implications for the performance of FRP retrofitted structural components.

Fig 1. FRP wrapped Columns as retrofit for bridge (Source: Wikipedia)

Epoxy resins are extensively used in composites as bonding adhesives, which has the potential role in retrofitting application since the debonding of epoxy matrix due to moisture attack causes the inactivation of load carrying capacity of FRPs. The schematic illustration of debonding failure of epoxy matrix due to moisture penetration is shown in Fig 2. Hence, intensive care has to be taken to tailor the epoxy resin in order to gain the full potential of FRP applications towards retrofitting of bridges. Bridges are the most sensitive structures, where the combination of unexpected loads as well as attack of aggressive ions play a negative factor towards collapse of them. As far as epoxy is concerned, a wide range of building blocks are used during polymerization and different cross-linking chemicals are generally employed [1-3]. Since the concrete columns are inorganic in

nature, compatibility and contact issues arise, while wrapping the fiber reinforcements, as the epoxy resin binder is purely organic in nature. Recent developments in the field of polymer nanocomposite after arrival of nanotechnology, it is possible to re-engineer or tailor the epoxy matrix by using compatible nano particles.

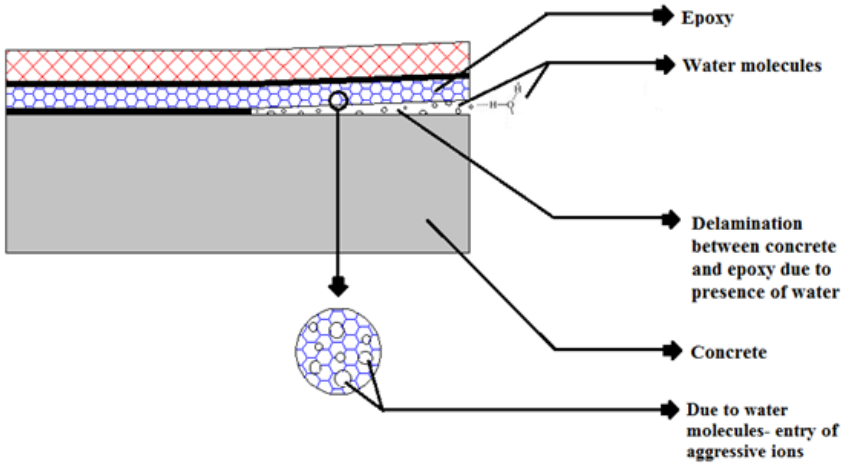


Fig 2. A Schematic illustration of delamination modes of FRP-Fiber/Concrete interface due to moisture penetration

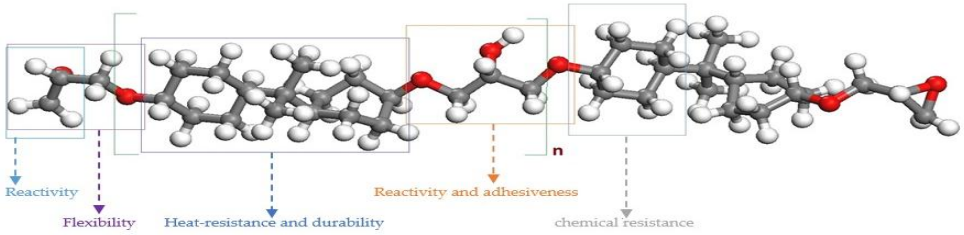
Polymer matrix are modified by adding nanoparticles, nanofibers and nanotubes as an additional phase into the epoxy resins by many means to improve further the functionalities such as toughness, damping, interlaminar crack propagation, elastic modulus, curing, surface wetting [3,4] etc. Chen et al. [5] concluded that small wt.% of nanosilica particle can increase the fracture toughness of epoxy resin compared to neat epoxy and stated that the improvement is less significant at larger weight fraction. When the silica-modified epoxy was adopted as matrices in the fabrication of fibre composites, the mechanical properties of the fibre composites increased accordingly. Ozkan et al. [6] reported that in the modified nanocomposite, shear strength increased due to interfacial presence of the nanoparticles. Hence, the possible alteration of cross-linking and molecular structure properties of the polymer in the immediate vicinity of the interface is evident. The effect of particle aspect ratio, particle modulus, and interparticle distance on the strengthening of particle-reinforced polymer was studied by Zhao and Hoa et al. [7]. Finite element analysis is used to confirm the mechanics of nano composites. Many authors reported that inclusion of nanosilica increased the fracture toughness of the epoxy matrices.

In this present study, it is aimed to functionally modify the epoxy matrix by using nano SiO_2 by possible means. Micro-analytical characterisation studies such as XRD, FT-IR, SEM, Surface area analysis, TG/DTA have been conducted to confirm the cross-link of nano SiO_2 at the epoxy backbone and to study the nanocomposite action of epoxy resin.

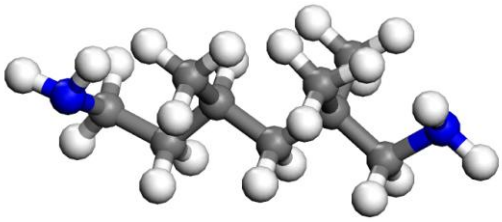
2. Experimental Investigations

2.1. Materials

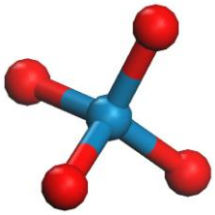
The epoxy resin and curing agent used are Diglycidyl ether of Bisphenol-A (Epichlorohydrin) with average molecular weight of ≤ 700 g/mole and Trimethylhexane-1,6-diamine with molecular weight of 158,29 g/mole, respectively. The ratio of resin and hardener is 4:1. Silica nanoparticle with an average size of 80 nm and a specific surface area of 200m^2/g is supplied by M/s Nanostructured and Amorphous Materials, USA. The 3D chemical structure of epoxy, curing agent, nano SiO_2 are shown in Fig 3. The highlighted potions in Fig 3a indicates the phsico-chemical functions of each moities present in the epoxy resin.



a) Bisphenol-A (Epichlorohydrin) type of epoxy resin



b) Trimethylhexane-1,6-diamine curing agent



c) Nano SiO_2

Fig. 3. Chemical structure of epoxy, curing agent and nano SiO_2

2.2. Surface functionalization of Epoxy resin with Nano-SiO_2 by Ultrasonication method

The required amount of precursor materials are weighed and subjected for sequential polymerization reaction. Epoxy composites are prepared by mixing the pre-weighed quantities of epoxy with and without silica nanoparticles in the ratio of 5 wt.% in mechanical stirrer at 70 °C for 3h. Then the mixture is kept under ultra-sonication for 2h. Afterwards, the compounds are heated to 80 °C and blended with the curing agent and subjected to vacuum de-gassing to remove moisture. The as prepared nano-composites are characterized to confirm the effect of functional modification.

3. Results and Discussions

3.1. XRD Analysis

XRD of nano SiO_2, neat and nano modified epoxy resin are collected by D2 PHASER (Bruker AXS Inc., USA) desk top XRD. The XRD spectrum for the same is shown in Fig 4. The amorphous nature of nano SiO_2 is confirmed through the corresponding spectrum. From this analysis, it is clear that the addition of nano particle greatly influenced the resin properties as the diffraction pattern of the respective spectrum is significantly altered. Further, it confirms the reaction of nano SiO_2 with epoxy backbone, as it influences the characteristic of cubic crystalline of $2\theta = 20.5°$, 26.3°, 29.1, 49.8° and 67.8° and d-space of the neat epoxy matrix.

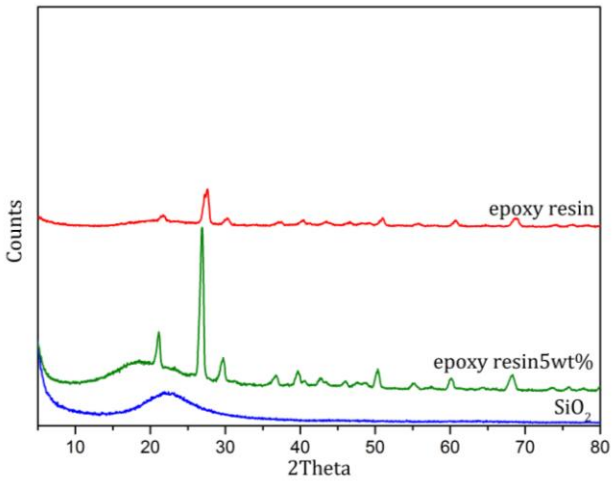


Fig 4. XRD pattern of epoxy, silica nanoparticle and epoxy resin/silica nanocomposite materials

3.2. FT-IR analysis

FT-IR spectroscopy is used to characterize the functional group of materials. The FT-IR spectra for the precursor materials and nano modified polymer composites are obtained in the frequency region of 4000-400 cm^{-1} region. Fig 5 shows the IR spectra of nanosilica, neat and modified epoxy resin. A strong band around 1085-1200 cm^{-1}, and 467 cm^{-1} confirms the siloxane (Si–O-Si) stretching absorption of nanosilica. For both neat and modified epoxy resins, the band features at 1800, 1370 and 1510 cm^{-1}, 1250 cm^{-1} are due to C=O stretching and C–O stretching vibrations, respectively. These C=O and C–O bands suggest the presence of O–C=O (ester) components. A broad H–O–H bending band around 1635 cm^{-1} and 1465 cm^{-1} can be due to aliphatic C–H bending for neat epoxy. In the case of epoxy resin containing 5 wt.% nano-SiO_2 powder the band at 1085 cm^{-1}, representing the dissymmetry flexible vibration of linear Si–O–Si, which is evident for the attachment of SiO_2 into the polymer backbone. Also, the absence of bending band for water molecule at 1080 - 1100 confirms the hydrophobic nature of modified epoxy resin. Further, the band at 3100 cm^{-1} to 3600 cm^{-1} represent the presence of -OH group and three absorption features aliphatic C–H are represented by stretching mode at 2965, 2935, and 2875 cm^{-1}. The 2965 and 2875 cm^{-1} peaks are due to asymmetric and symmetric stretching absorptions of CH_3, respectively.

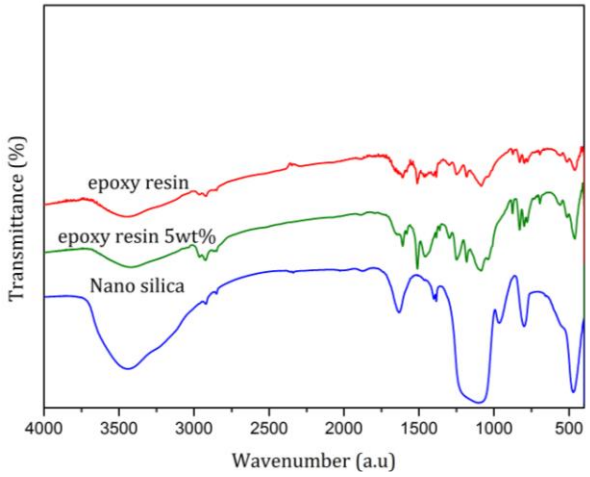


Fig 5. FT-IR spectra of epoxy, silica nanoparticle and epoxy resin/silica nanocomposite materials 5wt%

4.4. SEM

SEM analysis is conducted to examine the morphology of the fracture surfaces of the neat epoxy and modified epoxy as shown in Fig 6. From Fig 6, it is evident that the highly strengthened zones are populated evenly on the modified epoxy due to the filler effect of SiO_2 which is absent in neat epoxy morphology. This effect directly confirms the attachment of nano particles at the backbone of epoxy polymer. Furher, the confinement also very dense in the modified matrix. As the compact zone is formed, it will definitely act against moisture since the backbone is altered by hydrophobic moiety.

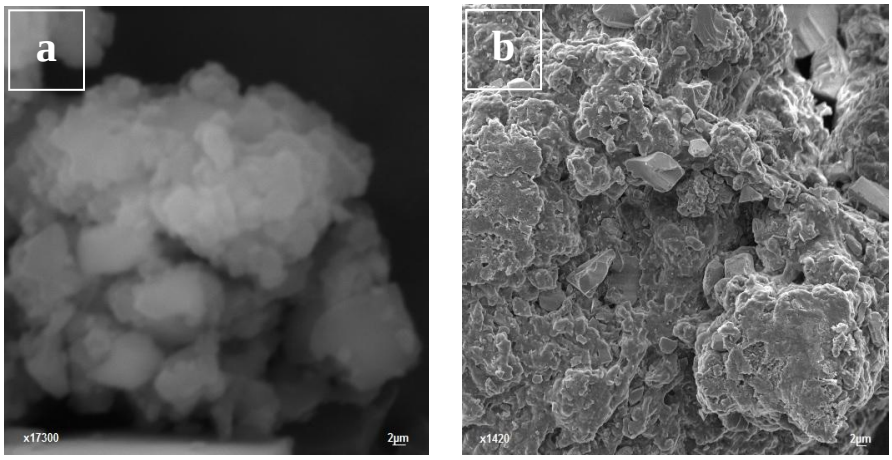


Fig 6. SEM micrographs of fractured surfaces of (a) neat epoxy and (b) modified epoxy

4.5. BET - Surface Area Analysis

Surface area is the important parameter, which determines the reaction rate of all homogeneous and heterogeneous materials. As for as the pores are concerned, it is important to proportionality alter or reduce them to have stable and energy minimized system. The surface areas of the neat epoxy, nano SiO_2 and epoxy/nanocomposite are shown in Table 1 and the micropore analysis of the same is shown in Fig 7. It is evident from this analysis that the surface area is decreased for the nano modified composite, which depicts the reaction of SiO_2 with epoxy polymer. Micropore analysis confirms that as the pore volume reduced and the matrix toughening mechanism is proved, which directly indicates the backbone alteration in epoxy.

Table 1 Results of Surface Area Analysis

Samples	**Surface Area (m^2/g)**							
	Multi-point	**BJH**		**DFT**	**DH**		**MP**	**V-t**
		Adsorp	**Desorp**		**Adsorp**	**Desorp**		
Neat Epoxy	42.864	19.637	19.925	15.446	20.598	20.891	42.864	1.814
SiO2	294.497	163.696	188.231	209.957	168.109	193.538	294.497	450.245
Epoxy nanocomposite	8.502	1.169	3.069	2.803	1.221	3.266	8.502	6.390

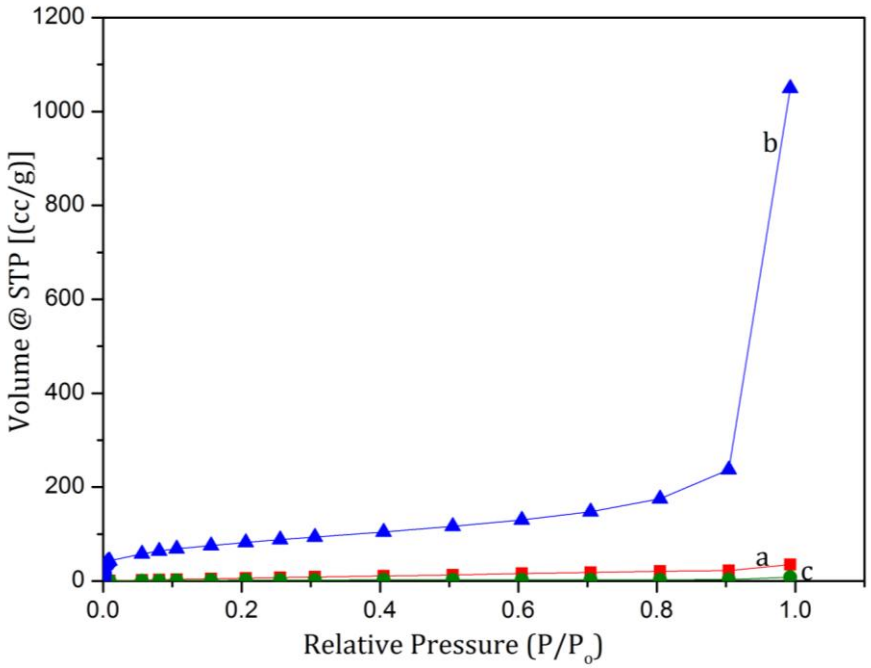


Fig 7. Micropore volume form linear isotherm plot (Adsorption) of N2 on (a) epoxy, (b) silica nanoparticle and (c) epoxy resin/silica nanocomposite materials 5wt% at 800 °C

Further, thermogravimetric analysis also confirms the reduction of weight loss at higher temperature for the modified resin. Based on the characterization studies conducted, the following structure as shown in Fig 8 is predicted for the nano modified epoxy or polymer modified nano composite.

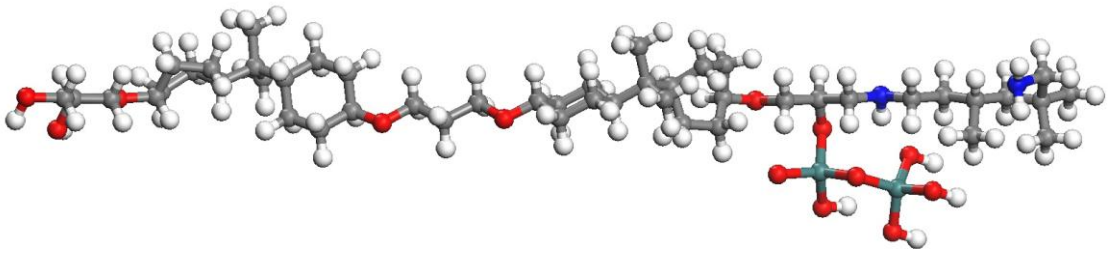


Fig 8. Modified epoxy resin with silica nanoparticle

Impact of nano modification of epoxy resin confirms the hydrophobic nature of the resultant mixture. Hence, it is expected that the as prepared polymer/nano composite can find much scope in the retrofitting applications of FRP for bridges. The dual purpose can be solved, i.e good bonding at interface and protecting structure from moisture attack, when we use the modified epoxy.

5. Conclusions

Nano modification of epoxy resin by SiO_2 is carried out by ultrasonication method. Micro-analytical characterization studies have been conducted to study the impact of nano modification. Based on the studies conducted, the possible interaction of nano SiO_2 with epoxy resin is predicted. Due to the enhanced hydrophobic

nature, it is concluded that functionally modified epoxy-polymer nanocomposite can be an alternate binder for FRP retrofitting applications and to protect the structure from moisture attack as well.

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