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SURFACE FUNCTIONALIZED NANO NICKEL OXIDE/UNSATURATED POLYESTER COMPOSITES FOR ENGINEERING APPLICATIONS

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Abstract - Unsaturated polyester matrix (UPR) based composites were prepared by reinforcing acryloxy functionalized nano nickel oxide. The effect of surface functionalization of the nano filler on mechanical properties of the composites was evaluated by comparing the ultimate tensile strength, flexural strength and impact strength under pre and post functionalization conditions. The physico-chemical interaction between the filler and matrix was studied by using Fourier Transform Infrared Spectroscopy, surface morphology by Scanning Electron Microscopy. From the results of these characterizations, it was conceived that reinforcement of surface functionalized of nano nickel oxide/UPR composites showed better performance compared to neat UPR composites.

Keywords: Unsaturated polyester, nano nickel oxide, tensile strength, flexural strength, silane treatment

I. INTRODUCTION

Polymers and polymer based composites have been given careful consideration by researchers throughout the most recent two decades because of their uniqueness viz. generally ease and simplicity of preparing. But in terms of mechanical strength and thermal stability, polymers are inferior with respect to other designing materials, for example, metals and alloys [1] and consequently their usage for structural and non-structural applications has been limited to some degree [2]. To combat these issues, various modifications in the processing were adopted which include use of relevant chemical stabilizers, reinforcing polymer with different fillers and fibres or blending of different types of polymers to tailor mechanical and physical properties of polymers [3-4]. Polymer matrix composites with different fillers like fly ash [5], bentonite [6], nano silica [7-8], montmorillonite [9], nano clay [10-11], carbon nanotubes [12], ZnO [13-14], glass fibres [15], natural fibres [16], and cellulose [17] have been reported to a greater coverage. Nanomaterials reinforced polymer composites found to have considerable improvement in thermal and mechanical [18], flame retardancy [19] optical and electrical properties [20]. Unsaturated polyester resins are the most generally utilized thermoset for the making of a wide collection of items, including sterile product, channels, tanks, gratings and elite parts for the marine and car industry. Nano sized nickel oxide particles possess excellent surface characteristics and it has been used as photo catalyst [21] but its use as filler in polymer composites is not well established. In case of nano fillers, particle agglomeration is the challenging phenomenon that produce more stress concentrated areas in the composites due to poor interfacial adhesion [22]. Surface modification is one the most common strategy that is followed to improve the interfacial adhesion between polymer and filler [23]. With this foundation, this investigation begins with point of creating multifunctional unsaturated polyester based composites reinforced with nanoscale oxide of nickel.

II. MATERIALS AND METHODS

2.1 Materials

In this work, unsaturated polyisophthalic ester resin, predissolved in 30 % v/v styrene monomer was used as matrix of the composites. Methyl ethyl ketone peroxide (MEKP) was used as the catalyst and Cobalt Naphthenate was used as accelerator. The resin mix, catalys and accelerator were purchased from Vasavibala resins private limited, Chennai, Tamil Nadu, India and used as such without any further chemical modification. Nano nickel (II) oxide (average particle size <50 nm) was used as filler and 3-(trimethoxysilyl)-propylmethacrylate (MPS) for surface treatment of the filler. Both the filler and coupling agent were procured from M/s. Sigma Aldrich India (Pvt) Ltd and used as such without any further purification.

2.2 Surface functionalization of nano nickel oxide

The silane surface modification of nano nickel oxide was carried out as follows: 1%, 2% and 3% solutions of 3- (trimethoxysilyl)-propylmethacrylate (MPS) in ethanol were prepared and the pH of each of the solution was adjusted to 4.5 - 5.5 by adding dilute acetic acid. 0.5 g nano nickel oxide was stirred with the silane solution for about 5 minutes and allowed to dry at room temperature for 48 hours.

2.3 Fabrication of composites

UPR resin and nano nickel oxide with required formulations were mixed with 1.5 % by weight of each catalyst and accelerator and fabricated in the form plates by Open Lay-up Resin Transfer Moulding method. The resin mix was allowed to cure for about 25 minutes at room temperature and post cured by microwave irradiation (2.4 GHz) at 240W for 30 minutes. The cured composite sheets were cut by water jet cutting machine.

2.4 Characterization

The tensile properties of the composites, as per standard ASTM D-638 type – I and flexural properties, as per standard ASTM D790, were determined using Instron 3382 UT machine of capacity 250 KN with moving crosshead of 50 mm/min. The Izod impact strength of the unnotched specimens of the composites was determined as per ASTM D256 standard using Tinius Olsen IT406 Pendulum Impact tester with striking velocity of 5.45 m/s. The average (subjected to low standard deviation) of measurement of three specimens was taken as the final result. Further, the composites were characterised by FTIR between the range 4000 cm^{-1} to 400 cm^{-1} by using Alpha Brucker spectrometer with resolution 4 cm^{-1} at room temperature. The tensile fractured surface of the composites was examined by SEM JEOL JSM 6390 LV scanning electron microscope with resolution 3nm.

III. RESULTS AND DISCUSSION

In polymer matrix composites, reinforcement of nano sized particulates impact the properties to a larger extent, than the microscopic particulates, even on smaller loading [24]. With this consideration, nano nickel oxide filled unsaturated polyester composites were prepared containing 0.1 – 1.0 % by weight of NiO. Table 3.1 shows the results of mechanical properties of NiO/UPR composites:

Table 3.1 Mechanical properties of surface untreated NiO/UPR composites

Sample Code	% by wt. of UPR	% by wt. of Nano Nickel Oxide	Tensile Strength (MPa)	Tensile Modulus (GPa)	% Elongation at break	Flexural Strength (MPa)	Flexural Modulus (GPa)	Impact Strength (KJ/m^2)
UPR	100	0.0	33.56	1.24	2.7	59.22	2.32	2.61
UPR/N1	99.9	0.1	44.01	1.71	2.6	70.21	3.68	3.85
UPR/N2	99.8	0.2	46.65	1.87	2.5	71.56	3.71	3.87
UPR/N3	99.7	0.3	48.22	1.99	2.4	72.34	3.76	3.93
UPR/N4	99.6	0.4	49.78	2.16	2.3	73.39	3.93	4.11
UPR/N5	99.5	0.5	48.03	1.91	2.5	74.55	4.12	4.32
UPR/N6	99.4	0.6	47.21	1.88	2.5	75.68	4.24	4.14
UPR/N7	99.3	0.7	45.98	1.76	2.6	74.11	4.24	4.03
UPR/N8	99.2	0.8	43.32	1.69	2.6	73.41	4.01	3.88

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UPR/N9	99.1	0.9	43.88	1.58	2.8	72.15	3.92	3.79
UPR/N10	99	1.0	41.99	1.54	2.7	70.63	3.78	3.56

It could be observed, from the results, that even a small fraction of nano NiO reinforcement has improved the strength significantly. 0.1 % weight fraction of nano nickel oxide addition has aggrandized the tensile strength by 31%, tensile modulus by 38%. flexural strength b y 18.5% and about 58% enhancement in flexural modulus and 47.5 % improvement in impact strength. Further the addition of nano NiO lead to an anisotropic change in the strength and modulus. 0.4 % loading shows maximum tensile strength and modulus after which the further addition of nano NiO deteriorates the strength and modulus. Since the average particle size of the used nickel oxide was less than 50 nm, larger surface to volume ratio of the particles lead to particle agglomeration [25] even at smaller loading and thus the results. But the surface treatment of nanofiller could reduce this effect and the same may be inferred from the experimental outcomes shown in the table 3.2. followed by their graphical representations:

Table 3.2 Mechanical properties of surface treated NiO/UPR composites

Sample Code	% by wt. of UPR	% by wt. of Nano Nickel Oxide	% Conc. Of MPS	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Impact Strength (KJ/m^2)
UPR/NA1	99.5	0.5	1	54.69	2.61	78.65	4.84	4.55
UPR/NA2	99.5	0.5	2	56.63	2.72	79.34	5.12	4.78
UPR/NA3	99.5	0.5	3	57.01	2.73	80.33	5.17	4.81

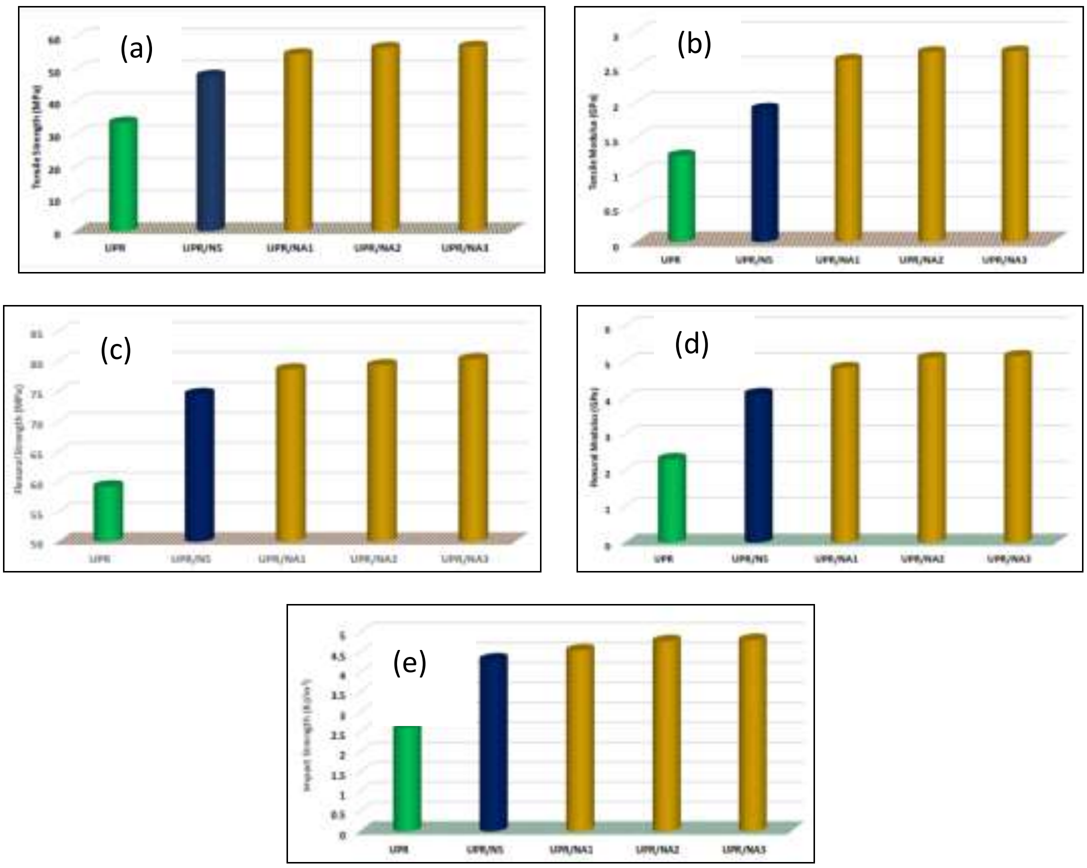

Figure 3.1 Effect of surface functionalization on (a) tensile strength (b) tensile modulus (c) flexural strength (d) flexural modulus (e) impact strength of NiO/UPR composites

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It is evident from figure 3.1 that the acryloxy functionalization of nano NiO shown an increment about 18.7 % in tensile strength, 42.9 % in tensile modulus, 7.7 % in flexural strength, 25.5 % in flexural modulus and 11.3 % hike in impact strength when compared to the UPR composite containing the same % by weight of untreated NiO. However, with respect to the neat composite, an increment of 69.9 % in tensile strength, 120 % in tensile modulus 35.6 % in flexural strength, 122.8 % in flexural modulus and 84.3 % in impact strength were observed. As the modulus is the ratio of stress to strain, from the experimental findings, it is inferred, from a drastic hike in modulus, that silane modification of nano particles reduce the failure strain that indicates uniform microstructure of the composites. The intensification of strength and modulus of silane functionalized NiO/UPR composites might be due to isolation of agglomerated nano particles, as represented pictorially in figure 3.2, that in turn improve particle /matrix adhesion.

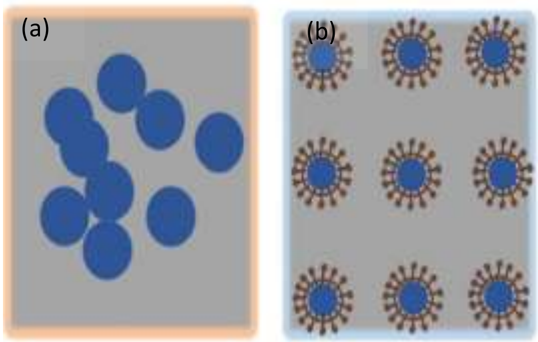

Figure 3.2 (a) Particle agglomeration before surface treatment (b) Isolation of particles after surface treatment

Figure 3.3 shows the results of FTIR characterization of composites and additives used. On comparing the FTIR spectra of untreated NiO (Figure 3.3 (c)) and that of acryloxy treated NiO (Figure 3.3 (d)), it is noted that a new and strong absorption peak is observed at 1039 cm^{-1} which is assigned to Si-O-Si bond and peak at 1126 cm^{-1} due to incorporation of Si –O – C bond [26]. This is a supporting evidence for the chemical interaction between nano particles and silane coupling agent and how the coupling process improves the interfacial adhesion between nano particle and polymer matrix.

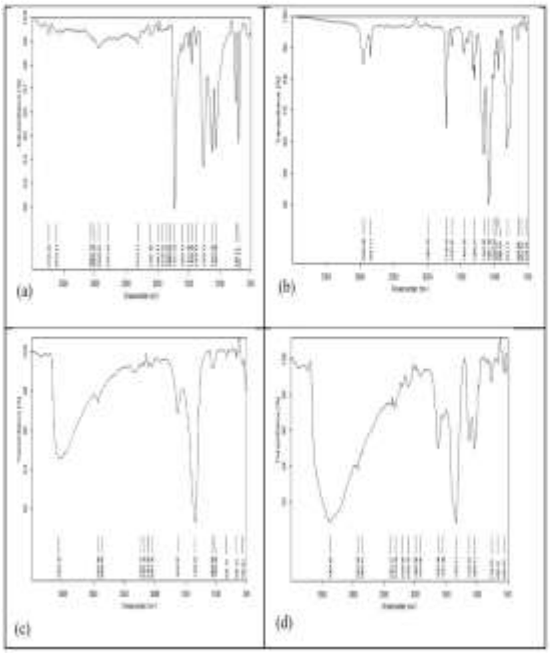

Figure 3.3 FTIR spectra of (a) Neat UPR (b) MPS (c) NiO (d) surface treated NiO

Figure 3.4 shows the SEM images tensile fractured specimens of NiO/UPR composites. It could be seen in figure 3.4 (b) that the pattern of fracture and surface shows a large number of failure propagation path and voids (indicated by arrows) and hence inferior strength of neat UPR composite. But in NiO filled UPR composites, the surface has no such voids and less number failure propagation paths as seen in figure 3.4 (c). Figure 3.4 (d) is image of UPR composite containing surface functionalised nano NiO. But the fracture pattern was almost uniform and linear propagation of failure paths in surface treated NiO/UPR composites. It has no elongation cavities and hence stiffer as concluded from mechanical characterization.

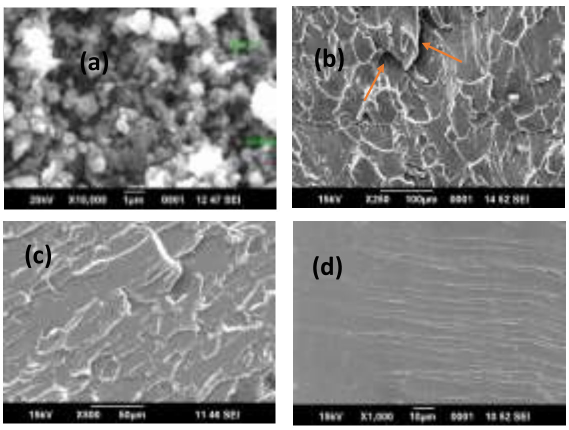

Figure 3.4 SEM image of (a) Nano NiO and tensile fractured surface of (b) neat UPR composite (c) UPR/N5 (d) UPR/NA3

IV. CONCLUSION

Nano nickel (II) oxide reinforced unsaturated polyester matrix composites were fabricated by open lay-up resin transfer moulding and post cured by microwave irradiation. The fabricated composites were characterized by FTIR, SEM and their mechanical properties were determined as per ASTM standards. The experimental observations revealed that the mechanical properties of acryloxy functionalized NiO/UPR composites were superior than the neat UPR and surface untreated NiO/UPR composites. The aggrandizement in properties is attributed by the fact that silane treatment develops a physico-chemical interaction between nano NiO and silane that lead to uniform particle distribution in UPR matrix. The same were evidenced by the FTIR spectra and SEM images of tensile fractured surfaces of the composites.

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