IJCPS Science International Journal of Chemical and Petroleum Sciences
ISSN 2253-0932

UNSATURATED POLYESTER RESINS MODIFIED WITH CRESOL NOVOLAC EPOXY AND SILICA NANOPARTICLES: PROCESSING AND MECHANICAL PROPERTIES

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ABSTRACT

In current research, unsaturated polyester resins modified with Cresol Novolac Epoxy and silica nanoparticles studied extensively in order to analyze changes in the physical, mechanical and thermal properties. It has been shown that by incorporating the amount of in to the polymer, the mechanical (modulus, strength, tensile, bending), and morphological properties have been substantially improved. The properties of cross-linked nanocomposites were characterized by, transmission electron microscopy (TEM), Scaning Electron Microscopy (SEM) methods according to the measurement, these modified, nanocomposites have been shown the significant improvement in the morphological and mechanical properties for coating applications.

Keywords: *Epoxy Cresol Novolac Resin, Silica Nanoparticles, Unsaturated Polyester Resin.*

1. NTRODUCTION

Silica nanoparticles as fillers are mixed with epoxy phenol novolac (EPN) resin for cryogenic applications. These properties are obtained while silicon nanoparticles permeate into the polymer matrix and form cross-linked attachments [1, 2]. Industry requirement for thermoset materials with appropriate properties caused EPN resin is produced and its properties were modified. These resins can be used in electronic plates, bush making and many other structural components. To enhance the physical properties, EPN resin is strengthened using silica nanoparticles. Properties of resins were modified dramatically by using these additives which increase thermal resistance of sample. An insulator with proper mechanical and electrical properties can be obtained by utilizing this process [3, 4]. EPN resins are compatible with unsaturated polyester. When the process of mixing and baking completes, toughness and impact resistance of resin increases significantly. Titanium and silicon nanoparticles are usually used to improve the properties of EPN resins. EPN resins have a high impact strength, low moisture absorption and good heat and chemical resistance. Some of the

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disadvantages of these epoxy resins are their dark color and non-transparency. These resins are also fragile in the absence of fillers. Multi-component polymer network epoxy resins are formed by internal cross-linked polymer chains. The first reason which vindicates compatibility of epoxy resin with UPR[1] is their polarity [5, 6]. Terminal groups of hydroxyl and carboxyl groups in UPR which perform as a catalyst during the curing process of epoxy resin, cause an increase in the chain length. Cross-linked and created Hydroxyl groups in this reaction are able to react with the epoxy groups [7, 8]. Modifying the physical, mechanical and thermal properties of ECN resin to reduce failure was performed before. According to the given reports, increasing the amount of fillers causes a great improvement in some physical and mechanical properties of ECN resin such as bending modulus, bending strength, tensile modulus and tensile strength [9, 10]. The biodegradation of nanocomposite using the phenol Novolac epoxy and the unsaturated polyester resins was studied. The effects of a nanobioceramic (the egg shell nanoparticle) and natural polymers (starch and glycerin) on the water adsorption of nanocomposite samples and also biodegradation of nanocomposite samples under soil were investigated. The results cleared that water adsorption increased in presence of egg shellnanopar1ticles [11]. Since nanocomposites are widely used in many industries. Current research focuses on thermal, physical and mechanical properties of them. Besides that, surface morphology of these materials is studied. Results show that adding optimized percentages of nanoparticles to resin instigates better properties.

2. MATERIALS AND METHODS

Epoxy cresol novolac (ECN) resin purchased from Komeyl Chemical Company, unsaturated polyester resin, cobalt Naftenat and methyl ethyl ketone peroxide purchased from Chemical Industry of Bushehr-Iran Company were prepared. In this research silica nanoparticles having 60 nm diameters were used as filler. Firstly, ECN resin was mixed with silica nanoparticles using a mechanical mixer for 15 minutes. Then ECN resin containing silica nanoparticles was mixed with unsaturated polyester using sonication mixer. ECN resin was cooked at room temperature with methyl ethyl ketone as accelerator agent and peroxide dimethyl phthalate containing 60 percent peroxide as hardening compound. The weight percentages of ECN resin were 5, 10, 15 and 20%. Cooking process was performed at room temperature for 24 hours, followed by the final cooking at 80 °C for 3 hours. Mixture was stirred perfectly to obtain a homogeneous liquid. The provided samples were poured into a glass mold attached to the sample container in one side while the other side was connected to a vacuum pump. Vacuum oven should be used to eliminate the bubbles in the sample. After cooking, the samples at specified temperature and time were completely put in the oven, and afterwards samples were cut into specific sizes in order to perform some tests such as moisture absorption, tensile strength, SEM microscopy studies, FTIR and DSC. Figure.1 depicts the diagram of nanoparticle size (PSA) of the Sio_2 nanoparticles. The size of the nanoparticles is determines to be 60 nm .Table.1 shows composition of the samples. This process was performed for all samples. In Figure.2 we can see a view of samples manufacturing process. Also in Table.2 we can see Physical and mechanical properties of all composite samples.

[1] Unsaturated polyester resin

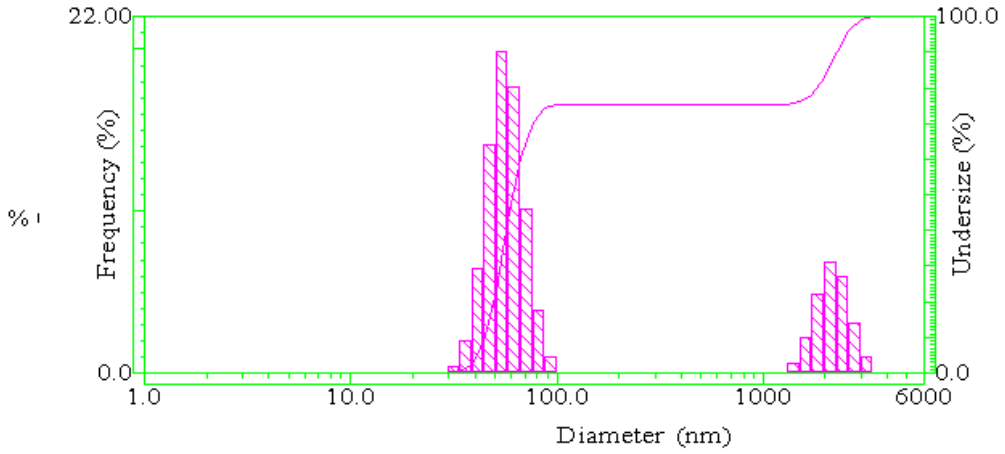

Fig.1. Particle Size Analyzer (PSA) nano SiO_2.

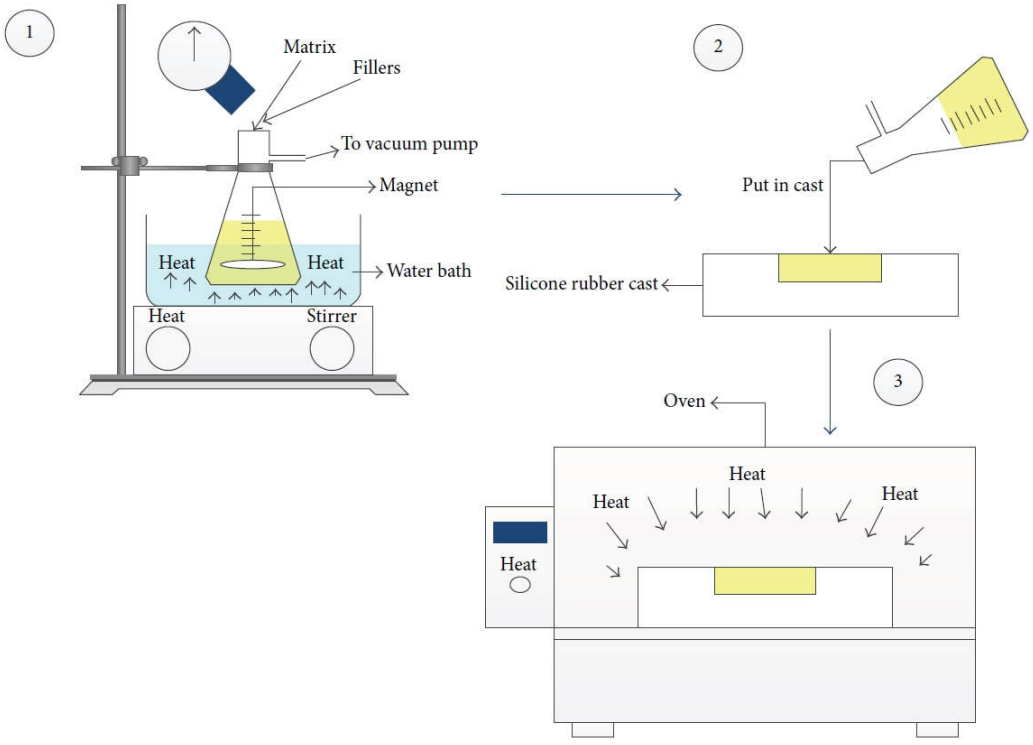

Fig.2. samples manufacturing process.

Table.1: Characteristics of provided samples

Samples Number	The amount of unsaturated polyester	The amount of ECN	The amount of silica nanoparticles
ECN/UPR/15%	50g	7.5g≈15%wt	-
ECN/UPR5%	50g	2.5g ≈ 5%wt	-
ECN/UPR5%/ SN1%	50g	2.5g ≈5%wt	1%wt
ECN/UPR5%/ SN3%	50g	2.5g ≈5%wt	3%wt
ECN/UPR5%/ SN5%	50g	2.5g ≈5%wt	5%wt
ECN/UPR10%/ SN1%	50g	5g ≈10%wt	1%wt
ECN/UPR10%/ SN3%	50g	5g ≈10%wt	3%wt
ECN/UPR10%/ SN5%	50g	5g ≈10%wt	5%wt
ECN/UPR20%/ SN1%	50g	10g ≈20%wt	1%wt
ECN/UPR20%/ SN3%	50g	10g ≈20%wt	3%wt
ECN/UPR20%/ SN5%	50g	10g ≈20%wt	5%wt

Table.2: Physical and mechanical properties of samples

samples ID	Tensile modulus (MPa)	Impact resistance (J/m)	Tensile strength (MPa)	Elongation at breaking point (%)
ECN/UPR/15%	67±2647	0.15±1.85	2.1±65	2.20±27.4
ECN/UPR5%	78±4499	0.13±1.70	4.9±62	0.02±0.6
ECN/UPR5%/ SN1%	84±2548	0.27±3.50	5.1±54	0.04±0.98
ECN/UPR5%/ SN3%	56±2924	0.31±3.22	4.5±59	0.03±0.75
ECN/UPR5%/ SN5%	72±3392	0.24±2.7	6.3±67	0.05±0.70
ECN/UPR10%/ SN1%	59±2439	0.56±6.51	3.9±52	0.10±1.40
ECN/UPR10%/ SN3%	74±2652	0.6±6.21	4.8±59	0.11±1.21
ECN/UPR10%/ SN5%	81±2948	0.39±4.97	5.6±63	0.04±1.87
ECN/UPR20%/ SN1%	51±2019	0.43±4.84	4.6±49	0.13±1.95
ECN/UPR20%/ SN3%	92±2226	0.38±4.21	49±53	0.14±1.72
ECN/UPR20%/ SN5%	69±2534	0.36±3.78	4.3±59	0.11±1.33

3. STUDY OF PHYSICAL AND MECHANICAL PROPERTIES

3.1. Impact Test

Results of Impact resistance test using Izod method are given in the figure.3. According to the table.2, the best result obtained by composite having 10wt% of ECN and 3wt% of nano-silica. Therefore, these percentages are proposed to be used in construction of such a nanocomposite. Increasing the amount of nano-Sio_2 instigates rise in sample's strength (impact resistance). At low percentages of nano-filler, this increased resistance is low and it reaches to the highest point at 3wt%. A reduction in strength observed at 5wt% of nanoparticles owing to accumulation of them causing tension concentration which results in reduction in sample's resistance against Impact.

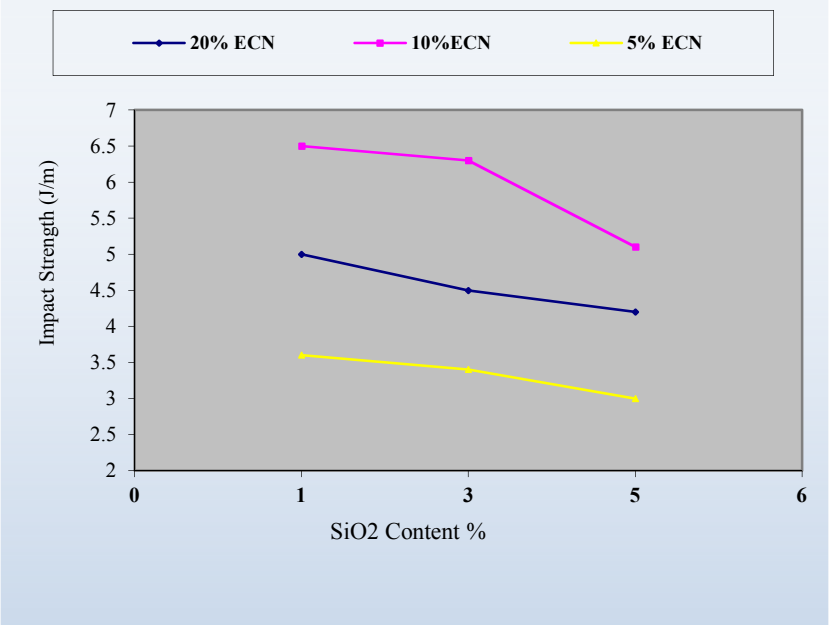

Fig.3. Effect of silica nanoparticles on impact resistance.

3.2. Young's module

Samples with 5, 10, 15 and 20wt% of EPC resin were analyzed to observe the effect of adding silica nanoparticles on the Young's module. Figure.4 depicts a noticeable increase in Young's modulus in the sample containing 5% EPN resin and 1% unsaturated polyester. This rising trend will continue with adding silica nanoparticles.

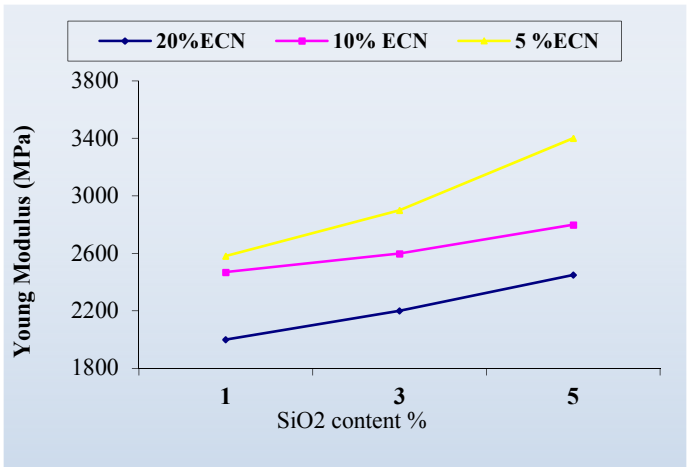

Fig.4. Effect of silica nanoparticles on Young's module.

3.3. Tensile test

It can be observed in Figure.5 that tensile strength increases with adding silica nanoparticles. Adding 1% nanoparticle resulted in a slight increase in sample's tensile strength. But when the weight percentage of nano SiO_2 reached to 3% by weight, final tensile increased significantly. By increasing Nano-particle to 5%, the tensile strength decreased.

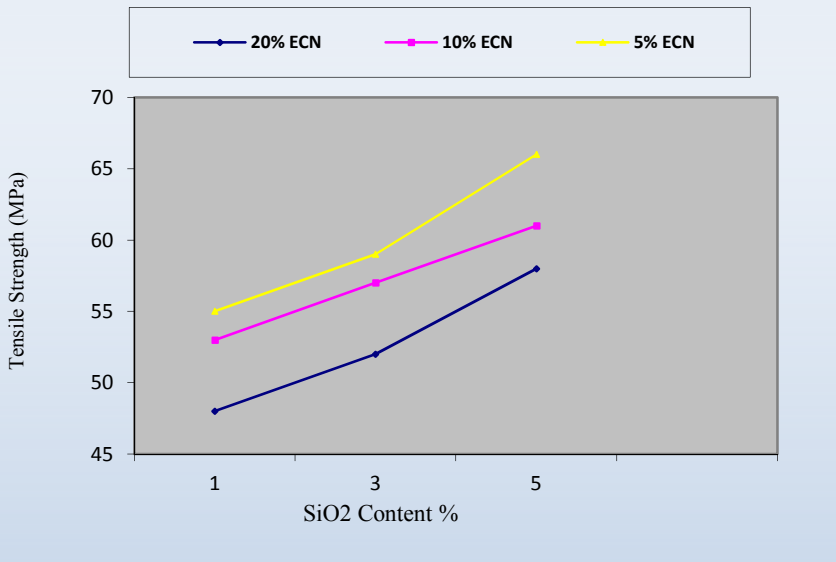

Fig.5. Effect of silica nanoparticles on tensile strength.

3.4. Elongation at breaking point

To observe the effect of silica nanoparticles on elongation at breaking point, ECN resin containing unsaturated polyester was used. Samples made of 5, 10 and 20wt% of ECN resin and 1, 3 and 5wt% of nano-silica were tested. Figure.6 shows that samples containing more ECN resin have greater elongation at breaking point.

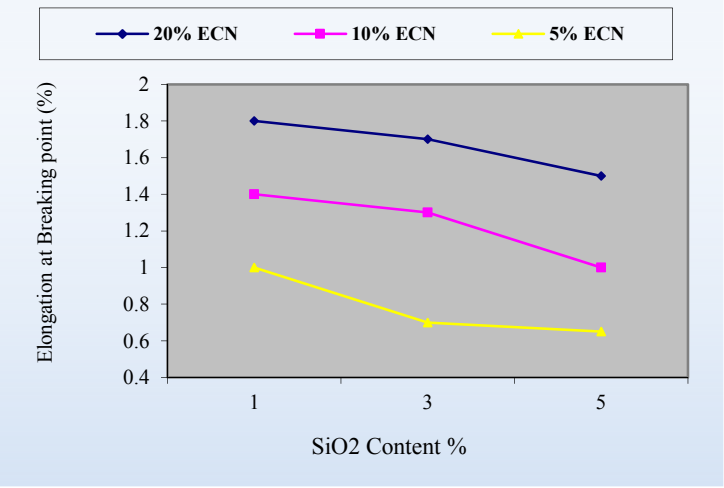

Fig 6. Effect of silica nanoparticles on elongation at breaking point.

In this section, effect of ECN resin percentage and unsaturated polyester on tensile properties and impact strength of blends will be discussed. According to the results in figures.7 and 8, it was found that increase in the percentage of ECN resin and unsaturated polyester contributes to decrease in Young's modulus and tensile strength. Also the results of impact test and elongation at breaking point have been shown in figure.9 and 10 respectively.

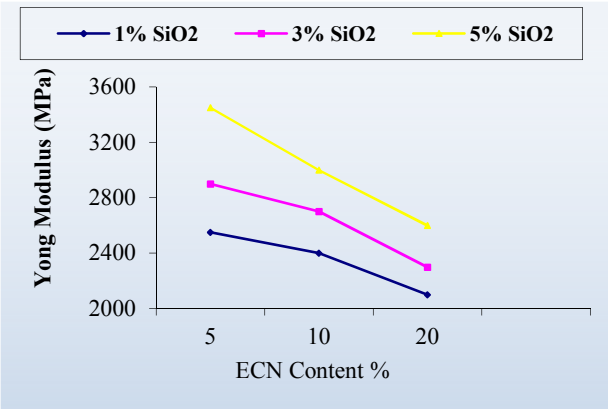

Fig.7. Effect of ECNR and unsaturated polyester on Young's module.

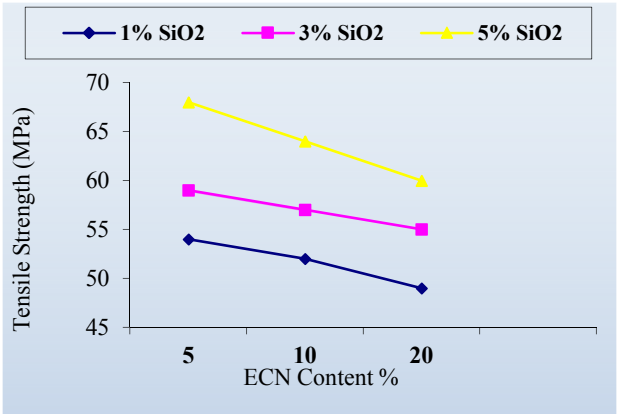

Fig.8. Effect of ECNR and unsaturated polyester on tensile Strength.

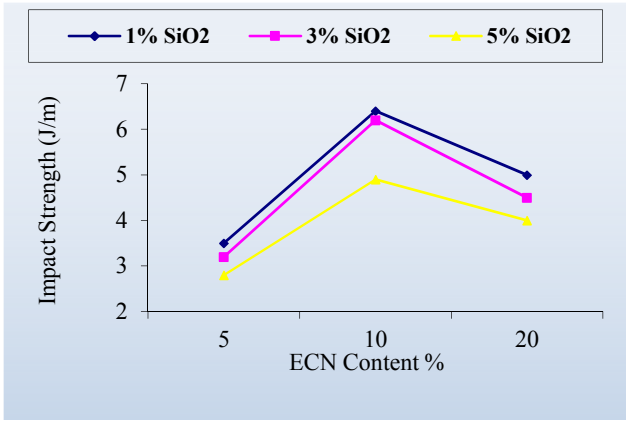

Fig.9. Effect of ECNR and unsaturated polyester on Impact Strength.

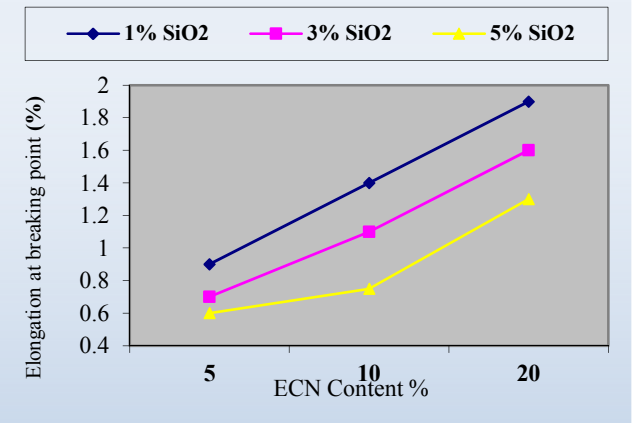

Fig.10. Effect of ECNR and unsaturated polyester on elongation at breaking point.

3.5. Test of abrasion resistance

Results of abrasion test with different weight percentages of nanoparticles are given in Table.3. Results show that increase in the percentage of nanoparticle brings about rise in abrasion resistance. At low percentages of nanoparticles (1%), no any noticeable change in abrasion resistance was observed. Increasing the amount of nano-filler to 5wt% leads to reduction in abrasion resistance. Adding nanoparticles to samples causes improvement in abrasion resistance because of the uniform distribution of them in the sample. Fillers are less effective at higher percentages of nanoparticles due to their tendency to accumulation and aggregation.

Table.3: Weight percentages of samples.

samples	ECN/UP R/15%	ECN/UP 5%	ECN/UP R5%/ SN1%	ECN/UP R5%/ SN3%	ECN/UP R5%/ SN5%	ECN/UPR1 0%/ SN1%	ECN/U PR10% / SN3%	ECN/U PR10% / SN5%	ECN/U PR20% / SN1%	ECN/U PR20% / SN3%	ECN/U PR20% / SN5%
Percentage of rubbed weight	11.63 ±0.01	10.48 ±0.01	8.26 ±0.01	5.87 ±0.01	6.13 ±0.01	4.55 ±0.01	2.19 ±0.01	3.34 ±0.01	5.67 ±0.01	4.11 ±0.01	3.23 ± 0.01

4. SPECTROSCOPY TEST (FTIR)

In Figure.11, part (a), the peak ranges between 1029 and 3503 cm^{-1} show the existence of hydroxyl groups and ranges between 1290 cm^{-1} and 3100 cm^{-1} depict the existence of hydroxyl group in the sample. In part (b), the presence of amine groups can be explained by peak ranges from 3371 cm^{-1} to 3461 cm^{-1}, and peak having wave number of 1605 cm^{-1} is due to presence of N-H bending group. CO groups are demonstrated by a peak with wave length of 1305 due to the presence of amine groups in epoxy phenol resin matrix and baked unsaturated polyester. In part (c), 3% silica nanoparticles were added to the composite which can be understood by peaks having wave numbers of 456 cm^{-1}, 1200 cm^{-1} ,1026 cm^{-1} and 829 cm^{-1}. In part (d), 5% silica nanoparticles were added to the composite which can be seen by a peak having wave number of 1132 cm^{-1} which shows the presence of Si-O-Si groups. Furthermore, wave numbers 828 cm^{-1} and 3055 cm^{-1} prove the presence of Si-O and Si-OH bending groups respectively.

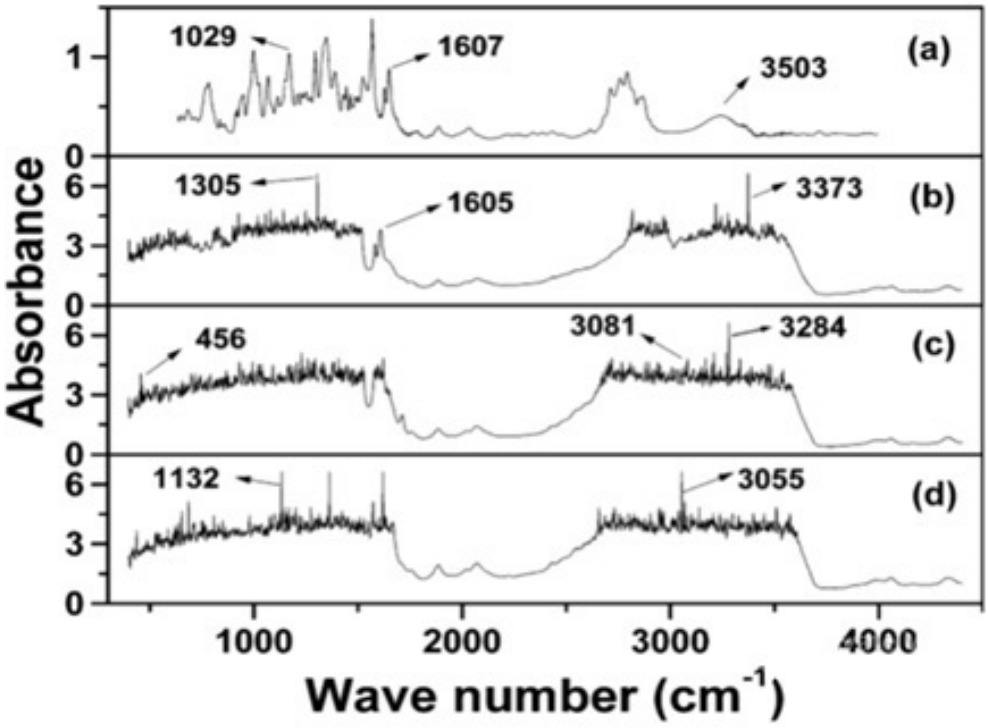

Fig.11. FTIR test. Part (a): ECN resin and unsaturated polyester. Part (b): ECN resin and baked unsaturated polyester with amine agent and 1%silica nanoparticles. Part (c): ECN resin and baked unsaturated polyester with amine agent and 3% silica nanoparticles. Part (d): ECN resin and baked unsaturated polyester with amine agent, and 5%silica nanoparticles.

5. SCANNING ELECTRON MICROSCOPY TEST (SEM)

To identify surface and distribution of nano-composite samples containing silica nanoparticles, SEM images were analyzed. Results obtained by surface morphology investigation of the samples are presented in the Figures.12-19.

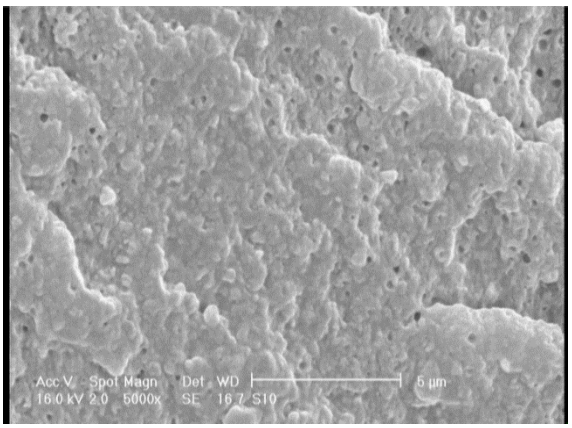

Fig.12. SEM image of epoxy resin containing unsaturated polyester resin (without nano-silica)

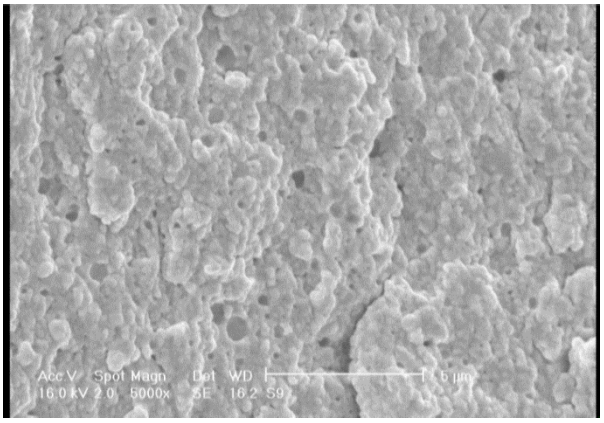

Fig.13. SEM image of sample containing 5wt% epoxy resin, unsaturated polyester resin, and 1wt% nano-silica

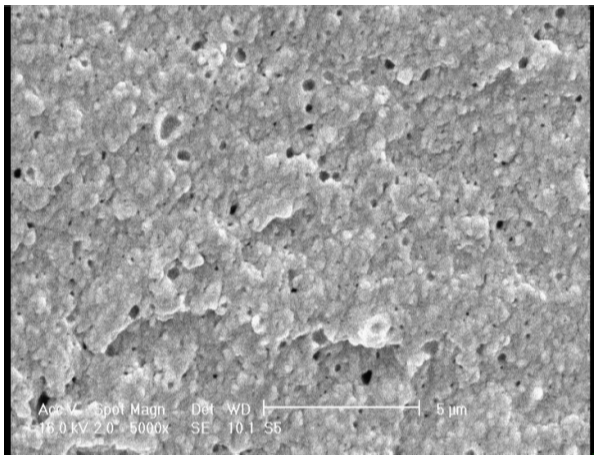

Fig.14. SEM image of sample containing 5wt% epoxy resin, unsaturated polyester resin, and 3wt% of nano-silica sample

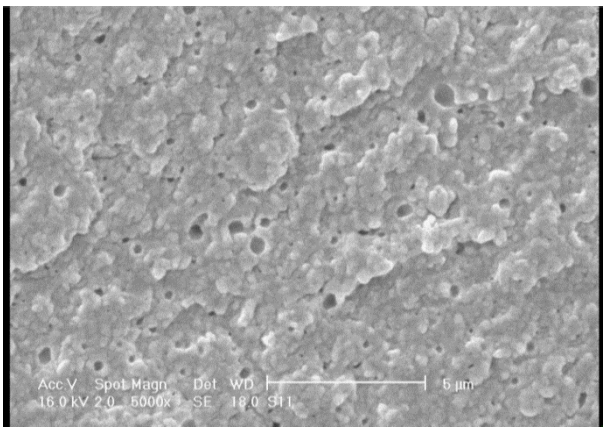

Fig.15. SEM image of sample containing 5wt% epoxy resin, unsaturated polyester resin, and 5wt% of nano-silica sample

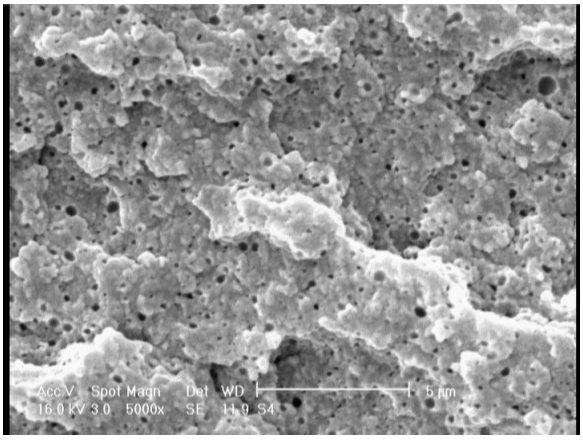

Fig.16. SEM image of sample containing 10wt% epoxy resin, unsaturated polyester resin, and 1wt% of nano-silica sample

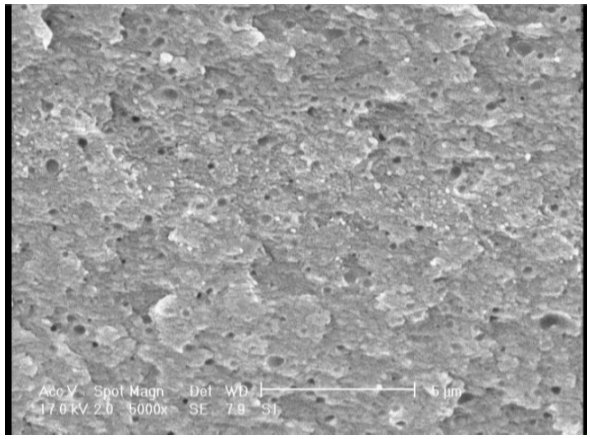

Fig.17. SEM image of sample containing 10wt% epoxy resin, unsaturated polyester resin, and 3wt% of nano-silica sample

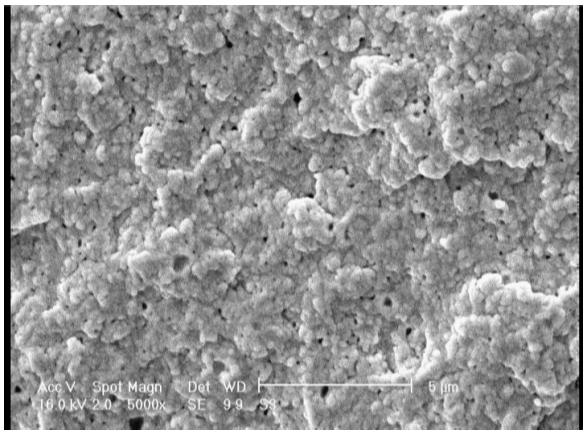

Fig.18. SEM image of sample containing 10wt% epoxy resin, unsaturated polyester resin, and 5wt% of nano-silica sample

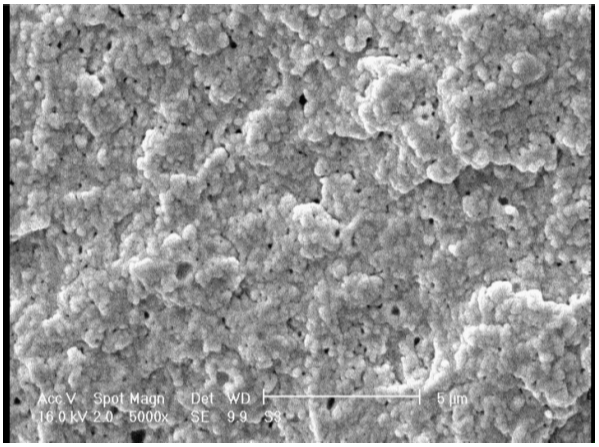

Fig.19. SEM image of sample containing 20wt% epoxy resin, unsaturated polyester resin, and 3wt% of nano-silica sample

6. TRANSMISSION ELECTRON MICROSCOPY (TEM) IMAGES

Figures.20, 21 and 22 depict the TEM images of samples with 1%, 3% and 5wt% of SiO_2 nanoparticles in resin epoxy respectively. Comparing these images demonstrates that sample with 3wt% nanoparticles having the best distribution shows the best performance. Although adding small amounts of nanoparticles (3%) may lead samples to have a better distribution, higher percentages (5%) may have an inverse effect. In other words, high percentages of nanoparticles results in agglomeration of them owing to attraction force of particles to each other in high concentrations. Therefore, adding high amounts of nanoparticle as hardening agent is not only ineffective, but also unfavorable.

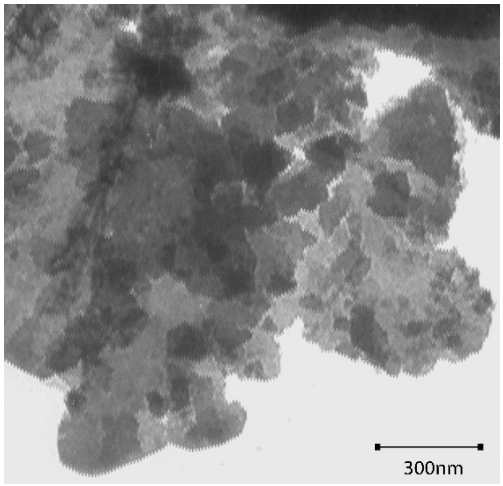

Fig.20. TEM images of sample containing 10wt% epoxy resin, unsaturated polyester resin, and 1wt% of nano-silica sample

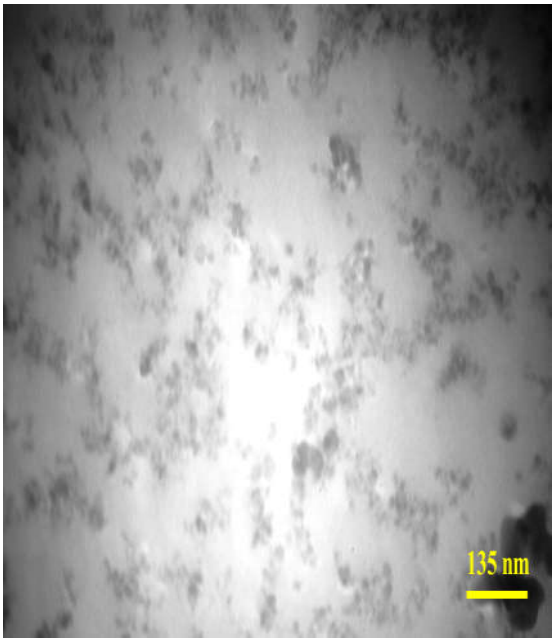

Fig.21. TEM images of sample containing 10wt% epoxy resin, unsaturated polyester resin, and 3wt% of nano-silica sample

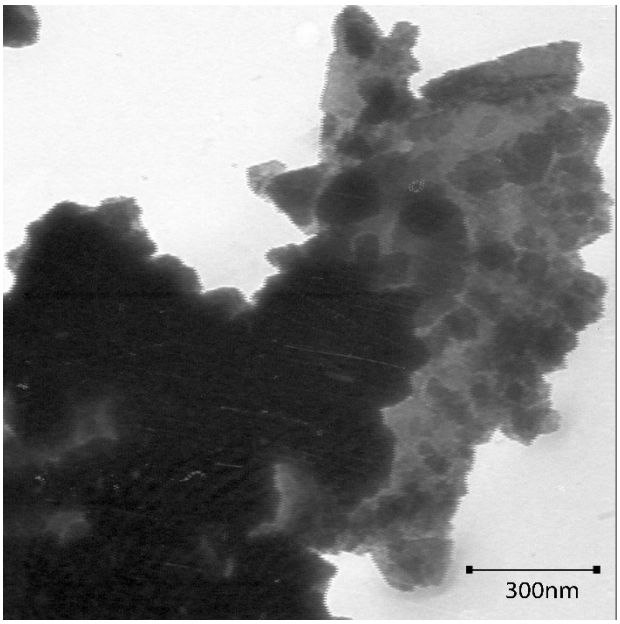

Fig.22. TEM images of sample containing 10wt% epoxy resin, unsaturated polyester resin, and 5wt% of nano-silica sample

7. CONCLUSION

In current research, ECN resin and silica nanoparticles are added to the mixture in order to modify unsaturated polyester resin. Results can be summarized as follows:

Combination of epoxy resin and unsaturated polyester resins containing silica nanoparticles resulted in a product having excellent strength and roughness. Characteristic of the product made by covering the first and the last layers with coating gels such as salinity of sea water at environmental conditions

have not any effect on it. Besides that, corrosion which occurs in marine conditions can not affect the nano-composites because these materials cannot be disintegrated spontaneity. Glass fibers (silica) and resins are not recoverable and therefore the environmental conditions have not any considerable influence on nano-composites. These nano-composites also have a high strength and stability than other composites. The obtained results show that ECN resins combined with unsaturated polyester resin and silica nanoparticles have greater physical and mechanical properties such as impact, bending and stretching.

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