



Phenol Novalac Epoxy-modified unsaturated polyester hybrid networks by Silica Nanoparticles/ and Cross linking with Silane Compounds

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Received: 02/04/2020

Accepted: 27/05/2020

Published: 20/06/2020

Abstract

In this study epoxy phenol novalac resin which consists of silica nanoparticles and unsaturated polyester resin linked to the Silane and cross linking to that structure and also parameters affecting the processes involved have been evaluated. Cross linking in phenol novalac epoxy resins effects on many properties such as thermal, electrical, mechanical and chemical attributes especially in elevated temperatures. Silane cross-linking's in phenol novalac epoxy resin with respect to other methods like proxiating, irradiation and utilization of Azo compounds, looks to be a very simple and low cost route, which makes it very encouraging for various industries. Unsaturated polyester resin is compatible with phenol novalac epoxy resin and also creates some cross-linking and as far as Trimethoxy Silane is added to the mentioned resin, its thermal, physical and mechanical properties are optimized. In this literature impact, tension, glass transition temperature, humidity absorption, FTIR and Scanning electron microscopy (SEM) tests were done and the results revealed that as the cross-linking occurs, tension in rupture region increases. This increase is more common at elevated temperatures. The growth in content of silica nanoparticles leads to a drop in water permeability of phenol novalac epoxy resin nanocomposite which contains unsaturated polyester resin.

Keywords: Phenol Novalac Epoxy resin, Trimethoxy Silane, Unsaturated Polyester resin

1 Introduction

The need for thermoset materials along with improved properties leads to manufacturing of phenol novalac epoxy resin and following improvements. This group of resins can be used in manufacturing of electronic boards, bushings and many other applications. In order to increase the physical properties, phenol novalac epoxy should be blended with silicon nanoparticles. Utilizing these additives ensures an improvement in electrical properties and by using this procedure yields an insulating material with good electrical and mechanical performance [1,2]. phenol novalac epoxy resins have the ability to mix and an obvious compatibility with unsaturated polyester. It has been seen that the stiffness and the impact resistance of resin after mixing and curing significantly increases. In order to improve phenol novalac epoxy resin properties such particle as titania and silicon nanoparticles is utilized. Phenol novalac epoxy resins have good impact resistance, low water absorption and also chemical and thermal resistance. One of the disadvantages of epoxy resins is that they are opaque, and also they are brittle without using any filler. The Epoxy resin which has been formed as a multicomponent polymer network is made of polymer chains internal cross-linking. The first reason for the compatibility between epoxy resin and UPR is that both of them are polar [3, 4]. Characteristics of samples has been shown in Table.1. End groups of carboxyl and hydroxyl act like catalysts within the UPR and they are just formed during the curing treatment of epoxy resin which leads to an elongation in chain length and cross-linking. The hydroxyl group formed during this process has the ability to react with the epoxide groups [5, 6]. In Table.2 physical and mechanical properties of samples has been shown.

In order to study effect of lost energy and the ability of epoxy and also fatigue resistance, some experiments have been done on Silane compounds, epoxy resins and glass which showed low molecular weight and fatigue resistance and also some cross-linking's have been formed [7]. Nowadays silicate and Silane compounds have been used in different categories such as dentistry, metals repair, tags, coatings, etc. [8]. Silane monomers are inactivated hydrophobic materials and in order to be activated they must be hydrolyzed with water and ethanol or acetic acid [9]. Silane compounds increase pastiness and also are widely used in laboratory simulation and improvement of dentistry programs [10, 11]. Nowadays use of tri methyl Acryl oxy propyl tri methyl oxy Silane after one hour of hydrolyzing for surface and parts is being in progress which shows elevated durability without any defects [12]. Silane compounds have the ability to store many bonds within the composite structure for a long period of time while the Silane monomer compounds form some cross-linkings among the chains shaped before. These compounds make the composite gain more mechanical and physical strength [13, 14]. Thickness of siloxane Film which has been coated in a silicate nano-composite substrate is a function of Concentration [15, 16].

2 Material and Methods

Phenol novalac Epoxy resin was purchased from komail kashan iran. Unsaturated polyester resin, Cobalt naphtenate and proxiade ethyl methyl ketone were obtained from bushehr chemical industries, Iran. Trimethoxy Silane which is a Silane compound was purchased from couchin company, india.

2.1 Methodology

During the cross-linking procedure with the assist of Silane in addition to proxiade as an initiator, another compound called Silane is needed as the main source of cross-linking. Selection of

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proxide should be done in a way that during the polymerization conditions it disperses among the polymer matrix which leads to a uniform bonding of the Silane groups to the polymer chains. At First, phenol novalac epoxy resin is being mixed with silicon nanoparticles and Trimethoxy Silane with the assistance of a mechanical mixer for 15 minutes. The phenol novalac epoxy resin which is now contains silicon nanoparticles and Trimethoxy Silane is blended with the unsaturated polyester. This mixing process is being handled with a sonication instrument. Phenol novalac epoxy resin has been cured at room temperature (by using of ethyl methyl ketone that contains 60% proxide and reaction accelerator). The amount of consumed Phenol novalac epoxy resin has been set to 5,10 and 15 % (w/w). The curing process is done for 24 hours with respect to the condition that curing has been done and after that the final step will be resumed at 80°C for 3 hours. The resulting blend should be mixed in order to yield a homogenous liquid. A better curing performance will be obtained by using of a di amine agent. The prepared samples will be moulded into a glass casting. These castings are attached to the samples container from one side and from the other side they are attached to the vacuum pump. The reason of utilizing of vacuum pump is to eliminate the existing bubbles in the samples. After the curing process, samples will be put into the oven at a specific temperature and for a certain period of time. The samples will be cut into specific slices to undergo different examinations such as water absorption, impact effect, tension, strength, SEM, DSC and FTIR.

Table 1. characteristics of samples.

Sample No	Content of unsaturated polyester	Epoxy Phenol novalac content	Trimethoxy Silane and nano silicon content
1	-	100 g	-
2	5%	100 g	-
3	10%	100 g	1%
4	10%	100 g	2%
5	10%	100 g	3%
6	10%	100 g	4%

Table 2. physical and mechanical properties of samples.

Epoxy EPN/UP/modified nano Silica	Tensile strength(MPa)	Impact strength(J/m)
100/00/00	67.3	102.43
100/05/00	64.9	107.62
100/10/01	62.3	119.50
100/10/02	73.6	137.72
100/10/03	78.9	146.83
100/10/04	74.8	135.43

3 Results and discussion

1.3 impact test (Izod)

In this research we applied the Izod impact test. By adding more silicon nanoparticles and Trimethoxy Silane as the agent to latticing the chains, make the chains stronger and also improve impact strength of those chains. Beside that as increasing silicon nanoparticle and Trimethoxy Silane content of samples, their impact strength increases in comparison with samples contain lower amount of silicon nanoparticles and Silane compounds which is the desired outcome of the experiments. The reason why this happens is about the strengthening effect of Silane and nanoparticles and the way that they infiltrate into the continuous phase of resin and moreover fill the pores of sample which yields an increase in flexibility of the samples and make them harder to

shatter. Although the impact strength of the samples increases, this reinforcement effect by applying 4 % (w/w) of nanoparticles has a contrariwise effect. Experimental evidences show this amount of nanoparticles play an important role in matrix fainting which is shown in figure (1, 2). One of the main problems of using silicon nanoparticles is particles agglomeration which mostly happens by addition of low nanoparticles contents such as 1, 2 or 3 % (w/w). Agglomeration problem can be eliminated by sonication and eventually the desired properties would be reached. As increasing nanoparticles content by a small increment from 3 to 4 % (w/w) the agglomeration issue remains unchanged and even by sonication of samples just the size distribution of mentioned particles will be smoothed and the problem still remains unsolved. Although high content of particles is the reason why the agglomeration happens and leads to a defect in particles surface this means a decrease in crack Energy and impact strength.

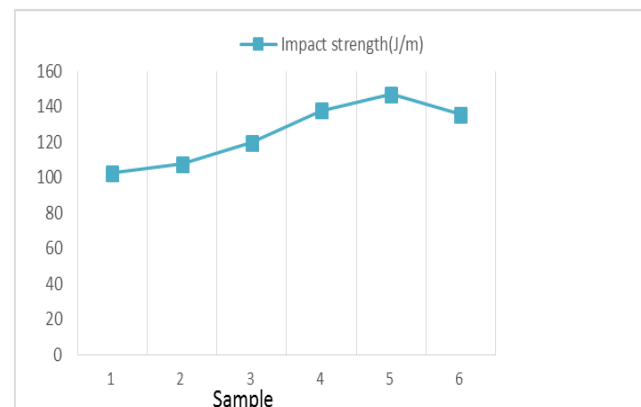


Figure 1: Izod impact diagram for samples with different silicon.

2.3 Water Absorption

A significant decrease in water absorption has been seen as a result of blending phenol novalac epoxy resin with unsaturated polyester and silicon nanoparticles. By increasing the silicon nanoparticles content, water permeability of the mentioned nano composite declines which is in fact the silicon nanoparticles that affect the permeability and make phenol novalac epoxy nanocomposite resin containing unsaturated polyester become hydrophobic (Table 3).

Table 3. Water absorption for phenol novalac epoxy resin/unsaturated polyester/Trimethoxy Silane hybrid nanocomposite.

Sample No.	Water Absorption
1	0.1441
2	0.1379
3	0.1103
4	0.1092
5	0.0947
6	0.0639

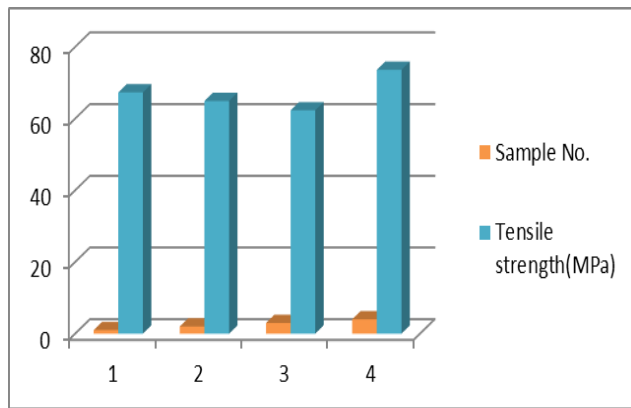


Figure 2: Water absorption diagram for phenol novalac epoxy containing unsaturated Polyester and Trimethoxy Silane nano composite.

3.3 Tensile Test

As the amount of silicon nanoparticles and Silane compounds increase and beside the physical entanglements and cross-linking, tensile strength of samples significantly increases. Tensile strength of samples increases by Utilizing the hanging Silane groups and silicon nanoparticles mounted on the chains of phenol novalac epoxy resin and unsaturated polyester (Figure 3). This phenomenon is caused by physical entanglement across the Silane groups. The amount of these entanglements increases as they increase in Number which in turn leads to elongation and an increment in Tensile strength. Sample No.1 contains pure epoxy phenol resin which has 67.3% response in tensile test. For sample No.2 the result is slightly lower and is about 64.9%. By using 2%(w/w) of silicon nanoparticle and Trimethoxy Silane in sample No.4 and the effect of cross linking's in amorphous phase reinforcement leads to an increase in Tensile strength and yields 73.6% for this sample. Sample No.5 which contains 3 % (w/w) of silicon nanoparticles and Trimethoxy Silane shows 78.9% as a result for this test. Addition of more silicon nanoparticles which is done for sample No.6 results a drop in tensile forces and shows 74.8% of tensile strength. More cross linking's in samples cause relative increase in stability of intertwined phenol novalac epoxy resin and unsaturated polyester chains which in turn cause samples to undergo more amount of strain. Growth of strain remains unless that the cross links block movement and slipping of chains across them. By the time that the cross links reach a maximum in numbers the chains slipping over each other descends and as a result the sample can undergo less amount of tensile before failure.

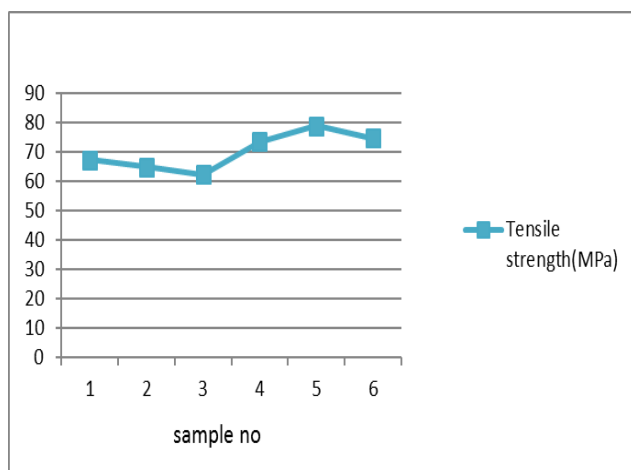


Figure 3: Tensile strength (MPa) diagram for samples with different silicon nanoparticles and Trimethoxy Silane with unsaturated polyester.

4.3 Glass transition temperature

Glass transition temperature for different samples has been shown in Figure 4 and Table 4 For Sample No.1 which contains phenol novalac epoxy resin Tg is about 166°C. For sample No.2 which contains 5% more of unsaturated polyester within its structure Tg drops clearly. For this sample the volume of cross linking's has been shrunk and also reaction accelerator has been reduced so that curing temperature drops. By the time that silicon nanoparticles and Trimethoxy Silane is added glass transition temperature increases again. This increment in Tg is because of the presence of silicon nanoparticles and cross linking's growth.

Table 4. Glass transition temperature.

Sample No.	Tg
1	166
2	149
3	140
4	153
5	163
6	165

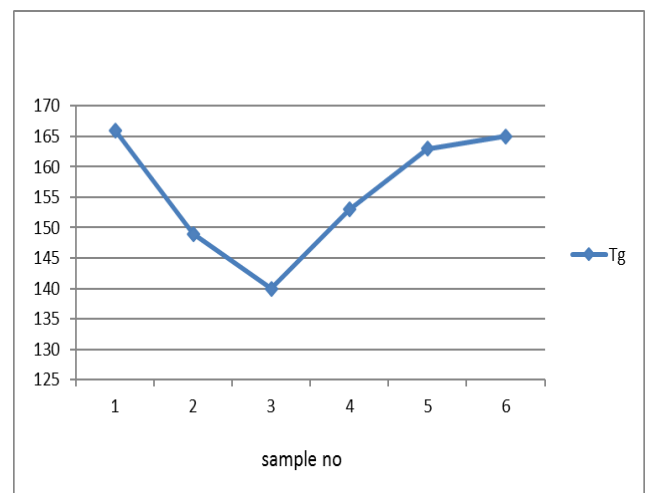


Figure 4: glass transition temperature Diagram.

Flexural strength of samples will increase by increasing the percent of Silicon and Trimethoxy Silane Nanoparticles. Adding 3% by weight of Silicon and Trimethoxy Silane Nanoparticles will be the optimum amount. Beyond this point, adding 4% for example, will decrease the flexural strength. These alterations are presented in Figure 5 and Table 5.

Table 5. Flexural strength of Epoxy Phenol Novalac Resin containing unsaturated polyester resin of Silicon and Trimethoxy Silane nanoparticles.

Sample No.	Flexural Strength
1	109.4
2	106.7
3	100.7
4	123.4
5	141.1
6	122.8

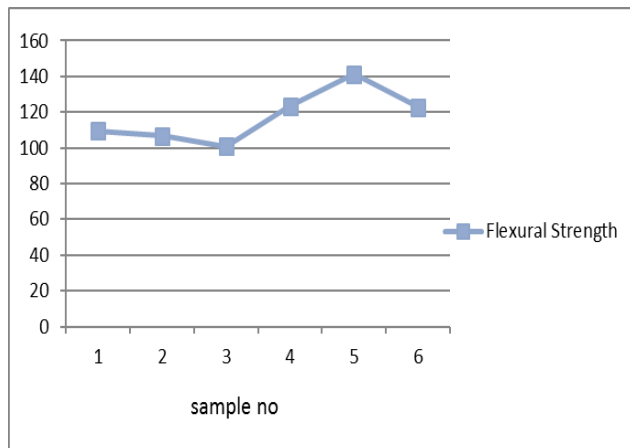


Figure 5: The chart of Flexural strength of Phenol Novalac Epoxy Resin containing unsaturated polyester resin of Silicon and Trimethoxy Silane nanoparticles.

5.3 FTIR Test

The FTIR apparatus of polymer and petroleum research center of Iran is used in this test. This apparatus covers the amplitude of 400 to 4000 cm^{-1} of infrared. This apparatus also is equipped with ATR (reflective method). A report has been recorded via infrared in Figure. 6 for two samples. Sample a, Silicon nanoparticles/Phenol Novalac Epoxy Resin/ unsaturated polyester resin and sample b, Silicon nanoparticles/ Phenol Novalac Epoxy Resin/ unsaturated polyester/ Trimethoxy Silane. In chart a, the maximum shows the 1000 cm^{-1} and in chart b, the bandwidth changes which is because of Silane groups available in nanocomposite chains. In this situation, bandwidth changes in the range of 3.100 cm^{-1} to 3.700 cm^{-1} . While this range molecules of water are absorbed by surface of Silicon.



Figure 6: FTIR test: Sample (a) Silicon nanoparticles/Phenol Novalac Epoxy Resin/ unsaturated polyester resin, Sample (b) Silicon nanoparticles/ Phenol Novalac Epoxy Resin/ unsaturated polyester/ Trimethoxy Silane.

6.3 Studies of Growing Electron Microscope

Survey of surface and distribution of nanocomposite samples containing Silicon nanoparticles and nanoparticles Titanium containing unsaturated polyester is done, using SEM analysis. Results from facial morphology study of samples are plotted in Figure 7 (a), (b), (c), and (d). Sample (a) is Phenol Novalac Epoxy Resin containing unsaturated polyester without nanoparticles. Sample (b) shows Phenol Novalac Epoxy Resin containing unsaturated polyester and Trimethoxy Silane and 1% by weight of Silicon nanoparticle. Sample (c) shows Phenol Novalac Epoxy Resin containing unsaturated polyester and trimethoxy Silane and 2% by weight of Silicon nanoparticle. Sample (d) shows Phenol Novalac Epoxy Resin containing unsaturated polyester and Trimethoxy Silane and 3% by weight of Silicon nanoparticle. Phenol Novalac Epoxy Resin containing unsaturated polyester does not include any nanoparticles itself. Many fractures were obvious on the composite surface. Perturbations and surface fractures were reduced by increasing percent of nanoparticles of Silicon and Trimethoxy Silane in the Epoxy Resin and the unsaturated polyester resin. In Fig. (c) and Fig. (d), distribution of Silicon and Trimethoxy Silane nanoparticles in the polymer matrix is shown. Silicon particles in Fig. (c) are spherical shaped with average size of 300 to 400 nanometers SEM image in Figure.8 shows (a) 1% by weight of silicon nanoparticle, (b) 2% by weight of silicon nanoparticle, (c) 3% by weight of silicon nanoparticle, and (d) 4% by weight of silicon nanoparticle.

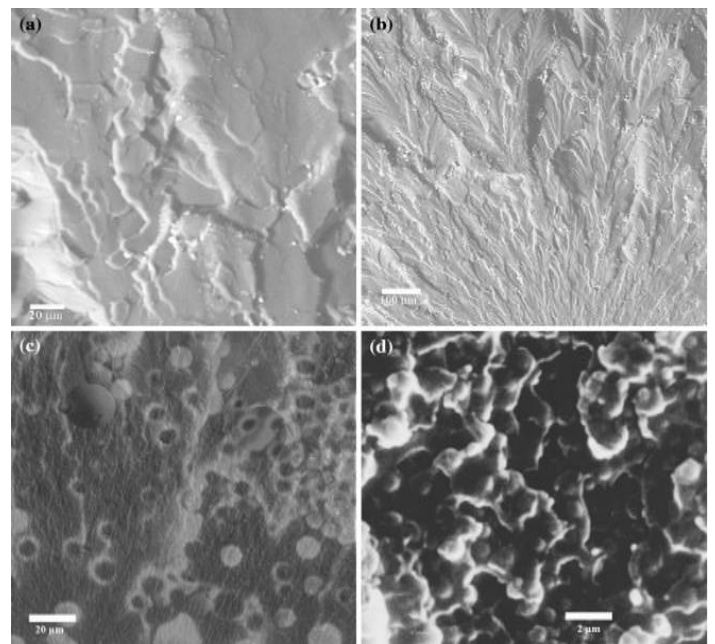


Figure 7: SEM image. (a) Phenol Novalac Epoxy Resin containing unsaturated polyester without nanoparticles, (b) Phenol Novalac Epoxy Resin containing unsaturated polyester and Tri methoxy Silane and 1% by weight of Silicon nanoparticle, (c) Phenol Novalac Epoxy Resin containing unsaturated polyester and Tri methoxy Silane and 2% by weight of Silicon nanoparticle (d) Phenol Novalac Epoxy Resin containing unsaturated polyester and Tri methoxy Silane and 3% by weight of Silicon nanoparticle.

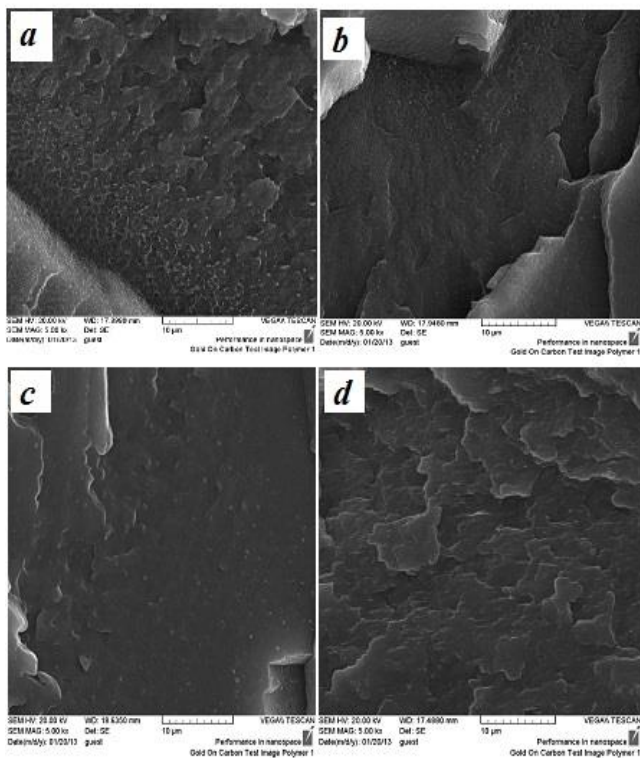


Figure 8: SEM image. (a) 1% by weight of silicon nanoparticle, (b) 2% by weight of silicon nanoparticle, (c) 3% by weight of silicon nanoparticle, (d) 4% by weight of silicon nanoparticle.

4 Conclusion

Transverse transplantation by Trimethoxy Silane, generally improves the physical and mechanical characteristics of nanocomposite of Phenol Novolac Epoxy Resin containing unsaturated polyester Resin, especially in high temperatures. Moisture absorption increases by increasing the percent of Silicon and Trimethoxy Silane nanoparticles to the composite structure. This matter can be a reason to anti-corrosion capability of this nanocomposite acting as cover in industry. Glass fiber or the Silicon and Resins are not recyclable. Thus, effect of surrounding conditions on this nanocomposite is negligible. This nanocomposite has more solidity.

Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

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