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Influence of nano graphene on water absorption in polyester/vinylester blend gel coats

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ABSTRACT

Water absorption characteristics of composite materials and gel coats are crucial for their applications in marine industry. The physical and mechanical properties of composite parts are influenced by moisture. Water absorption of five gel coat compositions based on epoxy vinylester resin and neopentylglycol unsaturated polyester resin and their blends was studied in this work. The influence of nanographene addition on the water absorption of these gel coats was also investigated. The results showed that epoxyvinylester resin had the lowest and neophentylglycol unsaturated polyester resin had the highest water absorption levels, and their blends, as expected, showed the same behavior. TEM, SEM and XRD were used to analyze and characterize the dispersion and distribution of nanographene particles in the polymer matrices. The results showed both dispersed and non-dispersed flakes in the polymer matrices. It was also shown that the addition of nanographene resulted in gel coats with lower water absorption levels.

Keywords

Gelcoat, Water absorption, Resin, Epoxy vinyl ester, Unsaturated polyester, Mixture rule, Composite materials, Nano grapheme.

1. Introduction

Immersion and floatation of a composite part in water and seawater has a significant influence on its appearance and mechanical properties. Therefore, application of gel coats on composite parts is a common procedure (See, Zhang and Richardson 2009), (CT. 2002). Fiber glass reinforced polyester resin has been widely used in manufacturing process for boat and automotive sectors (Kim, et al. 2011).

Gel coat resins are usually isophetalic or neopentylglycol isophetalic polyesters. These resins have a good hydrolytic stability, especially in moist environments. In addition to a good appearance, gel coats also affect the mechanical and chemical properties of the part. Gel coats protect the composite parts against fiber delamination and water absorption. Water absorption can result in chemical delamination such as hydrolysis of the matrix.

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Mechanical properties depend on the extent of decomposition after water absorption (Abdullah H 2000), (IMC. 1993). The most influential parameters on water absorption are polar and hydrophilic groups, position of these groups among hydrophobic groups, free volume and porosity (Zhao 2008). Composite parts are also sensitive to osmotic effect, when they are immersed in water. This can lead to delamination and blistering. Grump et al. (S. 1986) has studied the influential parameters on the blistering of laminates with gelcoats. They observed that all parts made of polyester showed delamination and blister formation when immersed in brine for a long time. The number and size of blisters depended on the gel coat thickness, pigmentation, fiber weight percentage and MEKP amount. Several works have been carried out on water penetration in coatings and behavior in composites as follows:

$$\frac{\partial \mathrm{c}}{\partial \mathrm{t}} = D\frac{\partial^2 C}{\partial x^2} \qquad (1)$$

Where D is the permeability, C is the concentration, t is the time and $\frac{\partial^2 C}{\partial x^2}$ is the second deviation of concentration changes at the distance of x from origin. See and co workers studied the water permeability of isophethalic acid polyester with addition of modified and unmodified nanoclay. Their result showed that the modified nanoclay composite had the lowest amount of water absorption. This is due to the fact that the modified nanoclay establishes a stronger bond with resin which prevents water molecules from penetrating into the composite. They suggested that the addition of nanoclay to the polyester resin resulted in a longer distance for water molecules passing through the matrix. In other work (Jawahar and Balasubramanian 2006), the influence of adding different amounts of nanoclay to polyester resin on water absorption of gel coat was investigated. They observed that with increasing the nanoclay concentration up to 2 weight percent the water penetration was decreased. They explained that the planer structure of layered nanoclay prevented the water molecules from penetrating into the matrix and the longer distance resulted in a lower penetration rate. Shah et al. (Shah 2001) Studied the water absorption of epoxy, vinylester and polyester resins in dionized water and brine. Their results exhibited typical Fickian behavior for all resins. Epoxy resin had the highest and vinylester had the lowest amount of water absorption. They correlated this to the chemical composition of resins. Existence of hydroxyl and amin groups in epoxy resin resulted in higher water absorption tendency. Epoxy group has the highest hydrophilicity and ester group has the lowest hydrophilicity among these functional groups. Zhang and co-workers (Zhang, See and Richardson 2009), investigated the composition of nanogel coats used in marine applications. They studied the influence of modified nanoclay on the isophetalic polyester gel coat. They observed that increasing nanoclay concentration resulted in better quality of coating with lower number of blisters. According to the literature (Swain 2013), (Ehsani M 2013), nano flakes have several benefits in polymer properties.

Nano flakes (e.g., nanograohene, nanoclay and glassflakes) provide improved properties in the direction of flakes due to their layered structure. Nano graphene has a great aspect ratio and layered structure which can increase the corrosive functionalities pass. This effect will be more pronounced when the flakes are positioned perpendicular to the direction of water molecules. There is no known research on the water absorption properties of neopentylglycol and epoxyvinylester gel coats, their blends and their nanograohene composites. This work aims to study five different gel coat systems prepared from polyester and vinylester resins. Also, nanographene was dispersed by ultrasonication and the resultant dispersion was studied using SEM and TEM. Then, the water absorption of pure gel coats, their blends and nanocomposites were studied.

2. Experimental

2.1. Materials

Epoxy vinylester resin based on bisphenol A (Chempuls 901) was obtained from Swancor Co., Taiwan. It has a viscosity of 450 cps and density of 1.04 g/cm3. Neopentylglycol unsaturated polyester resin (RESITAN UP-779) with a viscosity of 700-1200 cps and density of 1.1 g/cm3 was purchased from Resitan Co., Iran. Nonographene (XGn-M-25) was obtained from XGScience, USA (Table 1). Methylethyl ketone peroxide in di-methylphthalate solution (Akperox A60) as the curing initiator containing 10% active oxygen and 35% peroxide with a density of 1.17 g/cm3 was supplied from Akpakimya, Turkiye. Cobalt naphtanate (10% cobalt by weight) as the accelerating agent for speeding the curing action was supplied from Chekad, Iran.

Dimethylaniline (DMA) as the co-accelerator with a density of 0.956 g/cm3 was used for curing vinylester and supplied from Chekad, Iran. Aerosil was used as the thixotropic agent and supplied from Henan Xunyu Chemical Co., China. Anti-foaming agent was obtained from Chekad, Iran. Sample preparation

To prepare nanographene gel coats, 50 phr resin and 1 phr nanographene were mixed in an ultrasonic bath for 45 min (60 W, 59 Hz). Another mixture was prepared using 50 phr resin and 1 phr nanographene under mechanical stirring at 2000 rpm for 30 min. Neat gel coats were prepared by adding 100 phr resin in a beaker, following by addition of 2 phr aerosil and 1.5 phr anti-foaming agent to the resin and mixing for 45 min at 2000 rpm. Methyl ethyl ketone peroxide and cobalt naphtanate were added according to Tables 1-2 and 1-3. Finally, all mixtures were cast in a 30×30×3 mm^3 glass mold and left at room temperature for 24 h. Then, samples were de-molded and heated for an extra 2 h at 105 ˚C to complete the curing process.

2.2. Characterization

2.2.1.SEM

A TESCAN Brno SEM (VEGA 3 SBH) was employed to evaluate the nanographene dispersion and topology of the cross-section area of gel coats. Each sample was gold coated and experiments were carried out at 20 kV accelerating voltage.

Table 1: Characteristics of graphene nanoplatelets (technical data provided by the manufacturers)

Graphene type	**xGn-m-25**
Surface area (m2 g_1)	120-150
Density (g ml_1)	2.2
Oxygen content (%)	<1
Thickness (nm)	6-8
Diameter (μm)	25
Aspect ratio	3125-4167

Table 2 Codes and formulations of gel coat samples.

Sample code	**GVS**	**G3VN**	**GVN**	**GV3N**	**GNPG**
Epoxy vinylester (phr)	100	75	50	25	0
Neopantil glycol polyester (phr)	0	25	50	75	100
Aerosil (phr)	2	2	2	2	2
Anti bubble (phr)	1.5	1.5	1.5	1.5	1.5
MEKP (phr)	1.5	1.5	1.5	1.5	1.5
Accelerator Co 10% (phr)	0.3	0.2	0.2	0.2	0.2

Table 3 Codes and formulations of nanographene gel coat samples**.**

Sample code	**G3VN0.5XGn**	**G3VN1XGn**	**G3VN1.5XGn**	**GVS1XGn**	**GNPG1XGn**
Epoxy vinylester (phr)	75	75	75	100	0
Neopantilglycol polyester (phr)	25	25	25	0	100
Nanographene (phr)	0.5	1	1.5	1	1
Aerosil (phr)	1	1	1	1	1
Antibubble (phr)	1.5	1.5	1.5	1.5	1.5
MEKP (phr)	1.5	1.5	1.5	1.5	1.5
Accelerator Co 10% (phr)	0.1	0.1	0.1	0.1	0.025
DMA (phr)	0.06	0.06	0.06	0.08	-

2.2.2. XRD

A Siemens, D-5000 diffractometer, with Fe Kα radiator XRD was used to study the dispersion of nanographene layers. XRD spectra were collected in the 2θ range of 4° to 60°.

2.2.3. TEM

A Philips 208 S transmission electron microscope was used at an accelerating voltage of 150 kV to check the dispersion and size of nanoparticles.

2.2.4. Test method

Water absorption experiment was carried out according to D-570. The water absorption of samples was measured after immersion in dionized water (ASTMD570 2010). All samples were weighted before immersion. Then, they were placed in a dionized water container at 25 ˚C for 25 h. Surface of samples were dried using a towel and weighted immediately. Water absorption percentage as a function of time was calculated according to the Eq. (2):

$$Wt.(\%)(t) = 100 \times \frac{w_t - w_0}{w_0} \qquad (2)$$

Where $Wt\%$ is the weight change at time t, w_t is the weight of sample at time t and W_0 is the weight of dry polymer (before immersion).

3. Results and Discussion

3.1. XRD analysis

XRD was employed to evaluate the nanoflakes layering and dispersion. The XRD graphs of primary graphene powder XGn-m-25, gel coat G3VN and their nanocomposites are shown in Fig. 1. A sharp peak at 2θ of 26.4˚ (d-spacing~0.34 nm) corresponding to the d002 planner configuration of graphite is seen in Fig.1a (nanographene) (Sabzi, et al. 2013). As seen in Fig.1b, there is no peak in the XRD graph of neat gel coat (G3VN), which is due to its amorphous structure (Bora, Bharali, et al. 2013), (Bora, Gogoi, et al. 2013). Nanocomposites with the nanographene contents of 0.5, 1 and 1.5 phr show similar peaks at $2\theta = 26.4^\circ$ with increasing intensities correlated to the nanographene concentration. This indicates that the nanographene flakes are not totally dispersed.

3.2. Morphology

SEM was used to examine the quality of nanographene dispersion in the polymer matrix. Fig. 2(a) shows the SEM image of fractured surface of 0.5 phr nanographene-loaded gel coat. As seen, nanographene flakes are well-dispersed in the matrix. It is also seen that flakes are oriented in one direction.

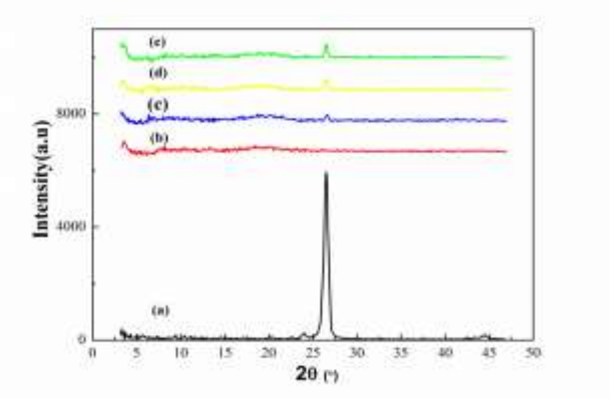

Fig. 1. XRD graphs of a) XGn-M-25 b) G3VN and their nanocomposites: c) 0.5 phr d) 1phr e) 1.5 phr.

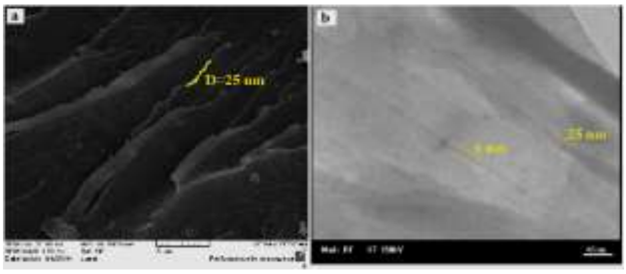

Fig. 2. SEM image of fractured surface of 0.5 phr nanographene-loaded gel coat (a) TEM image of G3VN gel coat containing 1 phr nanographene(b).

TEM was also used to study the dispersion and thickness of nanographene flakes.

Fig. 2 (b) shows the TEM image of G3VN gel coat containing 1 phr nanographene. This image shows the nanographene flakes with the thicknesses in the range of 6-25 nm, which are thicker than the thickness of individual nanographene flakes (6-8 nm) (specialchem4coatings 2009). This confirms the existence of multilayer nanographene structures in nanometer dimensions.

3.3. Water Absorption Properties

Fig. 3 shows the water absorption of epoxyvinyl ester (GVS), neopentyl glycol unsaturated polyester (GNPG), and their blends (25/75: G3VN, 50/50: GVN and 75/25: GV3N). As seen in Fig.3, the water absorption curves consist of three parts. In the first part, the water absorption rate is high and three are no much differences among the curves. Then, the water absorption rate tends to decrease and the differences among the curves become more pronounced. Finally, all the curves reach to a plateau region, which shows the saturated water absorption condition. According to Fig. 3, the GNPG gel coat due to the presence of hydrophilic groups in its chemical composition and because of its higher free volume shows higher water absorption compared to the GVS gel coat. Also, due to the high viscosity of GNPG, the probability of bubble formation is large during its preparation and its casting, resulting in higher water absorption.

The increase of neopentylglycol content in the blends resulted in higher water absorption level. Saturated water absorption of the blends was calculated using mixture rule. The saturated water absorption values calculated using mixture rule are close to those obtained from the experiments, indicating the blends structure do not have significant influence on the free volume (Table 2).

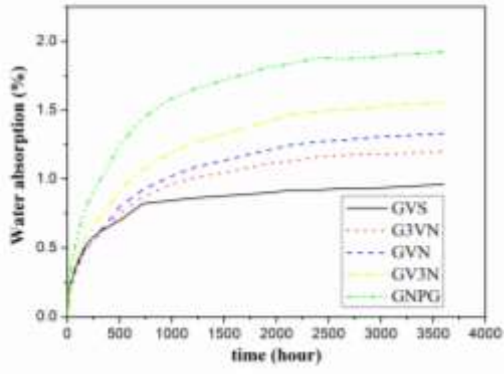

Fig.

Fig.3. Water absorption of gelcoats

The calculated (theoretical) and experimental water absorption values for different gel coats are listed in Table 1. Different water absorption trend was seen of the beginning compared with the final water absorption amounts. In the first few days, water absorption decreased gradually to the point that the water absorption of the G3VN exceeded that of GVS. Similar trend was seen for the other two blends. In the first part, the values calculated using the mixture rule were higher than the experimental values for all blends. The reduction in water in this part of the is considerable. This can be due to the formation of a specific structure as a result of blending two gel coats. A similar story has been seen for other polymers such as polyvinylalchol (PVOH). At the beginning, the water absorption rate is very low in this polymer, but it increases gradually until finally the polymer is fully dissolved in water (poval 2010). This is because of the strong hydrogen bonds between hydroxyl groups. So, hydroxyl group gather aside each other and surround the neighboring non-polar groups. In this case, it seems that the neopentyl glycol group has covered the vinylester polar groups in the blends. Because of lower water absorption of G3VN gel coat, it was chosen to study the effect of nanographene concentration on the water absorption of composites. Fig. 4 shows the water absorption curves for the G3VN gel coats containing 0.5, 1 and 1.5 phr nanographene. As seen, the addition of 0.5 phr nanographene has a significant influence on the water absorption.

This amount was lower for higher nanographene loaded composites. The nanocomposite containing 1 phr nanographene was used for further experiments. Fig. 5 shows the water absorption of GVS, GNPG, G3VN and their blend containing 1 phr nanographene. Due to the presence of nanographene, the higher water absorption rates observed for neat gel coats were not observed here.

Table2. Coding and formulation gelcoat samples

Sample code	**GVS**	**G3VN**	**GVN**	**GV3N**	**GNPG**
Unsaturated water absorption (experimental)	0.96	1.2	1.33	1.55	1.92
Unsaturated water absorption (Calculated)	-	1.1808	1.4208	1.6608	-

Table 3: The calculated (theoretical) and experimental values for water absorption of different gelcoats

Time (hour)	**GNPG (exp) (%)**	**GV3N (cal) (%)**	**GV3N (exp) (%)**	**GVN (cal) (%)**	**GV (exp) (%)**	**G3VN (cal) (%)**	**G3VN (exp) (%)**	**GVS (exp) (%)**
0	0	0	0	0	0	0	0	0
24	0.3	0.2784	0.23	0.2584	0.19	0.2384	0.2	0.22
48	0.42	0.3822	0.31	0.3472	0.27	0.3122	0.25	0.28
72	0.51	0.4641	0.38	0.4216	0.32	0.3791	0.31	0.34
96	0.59	0.536	0.44	0.486	0.37	0.436	0.35	0.39
168	0.78	0.7071	0.57	0.6396	0.49	0.5721	0.47	0.51
240	0.89	0.8036	0.65	0.7236	0.57	0.6436	0.54	0.57
336	1.02	0.9147	0.74	0.8172	0.64	0.7197	0.61	0.63
504	1.25	1.1015	0.92	0.964	0.8	0.8265	0.75	0.7
720	1.44	1.2726	1.06	1.1176	0.92	0.9626	0.87	0.82
960	1.57	1.3729	1.18	1.1904	1.01	1.0079	0.95	0.84
1200	1.65	1.4367	1.26	1.2392	1.08	1.0417	1.02	0.86
1920	1.81	1.5643	1.42	1.3368	1.21	1.1093	1.11	0.9
2160	1.84	1.5916	1.47	1.3616	1.25	1.1316	1.13	0.92
2400	1.88	1.6208	1.49	1.3808	1.27	1.1408	1.16	0.92
2640	1.87	1.6162	1.5	1.3812	1.28	1.1462	1.17	0.93
2880	1.88	1.6235	1.51	1.386	1.3	1.1485	1.18	0.93
3120	1.9	1.6408	1.54	1.4008	1.31	1.1608	1.18	0.94
3600	1.92	1.6608	1.55	1.4208	1.33	1.1808	1.2	0.96

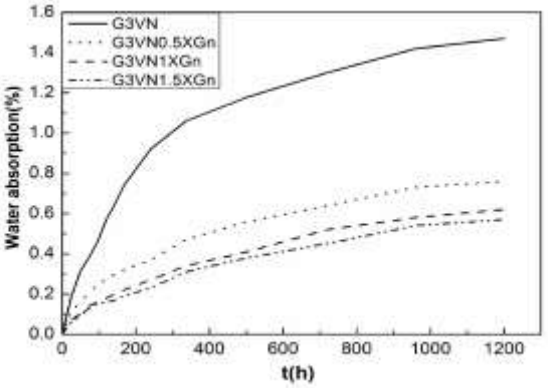

Fig.4. Water absorption of nanographene gel coat samples

Fig. 6 shows the water absorption curves of neat and nanographene loaded gel coats.

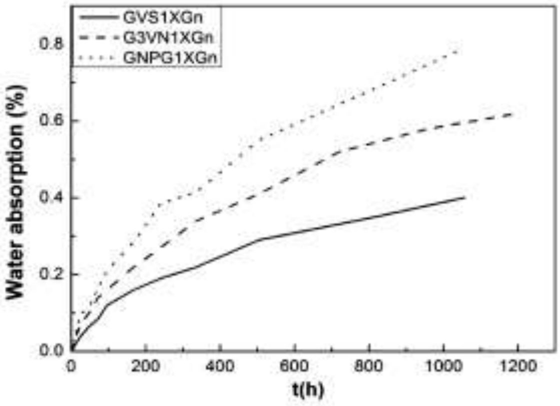

Fig. 5. Water absorption of water absorption of GVS, GNPG, G3VN and their blend containing 1 phr nanographene

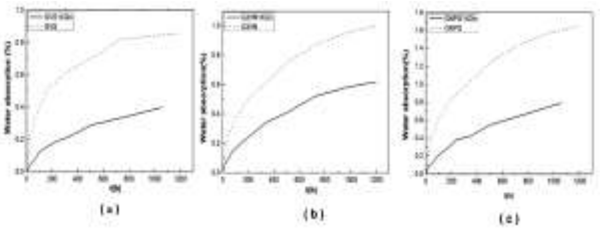

Fig. 6. water absorption curves of neat and nanographene loaded gel coats.

As seen in all cases, there are comparable differences between the water absorption of gel coats. This confirms that the nanographene flakes have a significant influence on the water absorption reduction.

This can be explained using the two following facts:

First, the travel distance of water molecules is longer in the presence of nanographene. According to the Fick's law:

$$\frac{\partial c}{\partial t} \propto \frac{\partial^2 c}{\partial x^2} \qquad (3)$$

It means that, at any time concentration at one point is function of the distance between that point to the interface. The concentration variation with the distance from interface is shown in Fig.7.

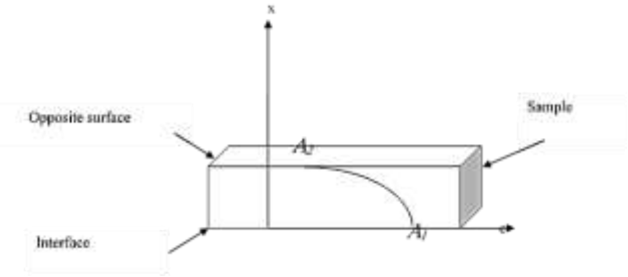

Fig.7. Concentration variation with the distance from interface

The highest and lowest solvent concentrations are at the points A_1 (interface) and A_2 (opposite surface), respectively. This is power law equation which can be represented as Eq. (4):

$$C_x \propto e^{(-a \times x)} \qquad (4)$$

Where a is a constant coefficient, x is the distance from interface, and C_x is the concentration at point x. Therefore, it can be concluded that by increasing the distance the solvent concentration is decreased. Nano flakes positioned perpendicular to the flow direction increase the distance from the interface significantly.

The second reason is the flow rate of water. (The amount of solvent that travels through a flow pass, which is the suface of the sample here, at a time) of sample with or without nanographene.

It is believed that the effective surface ($A_{effective}$) in the sample with nano flakes is getting smaller proportional to the unpermeable surface of nano flakes. If means that the effective surface of water absorption to the samples containing nanographene is smaller than A_{nano} ($A_{neat} = A_{nano} > A_{effective}$) (Fig. 9).

Considering the effective surface, the nanographene-loaded sample was similar to the neat sample, so, the pressure drop is the same in both the samples ($\Delta p = \Delta \acute{p}$), and due to the direct relation of pressure drop and velocity ($\Delta p \ \alpha \ V$), the water absorption velocity in the nanographene-loaded sample is equal to that in the neat sample ($V_{neat} = V_{nano}$). Therefore, the flow rate can be calculated as Eq. (5) and Eq. (6):

$$Q_{neat} = v_{neat} \times A_{neat} \qquad (5)$$

$$Q_{nano} = v_{nano} \times A_{effective} \qquad (6)$$

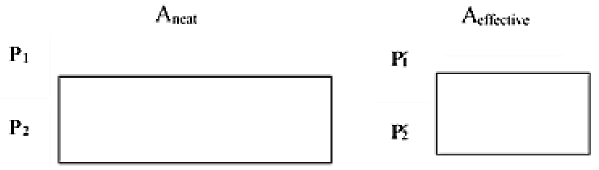

Fig. 8: Schematic of Surface of the neat gelcoat and Effective surface in the samples containing nanographene.

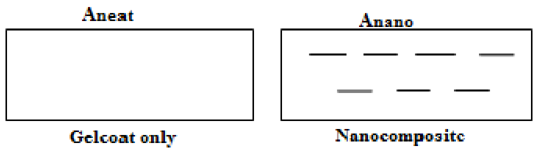

Fig. 9. Schematic of Surface of the neat gelcoat and Effective surface in the samples containing nanographene

According to these equations, the flow rate of nanographene-loaded sample is smaller than that of the neat sample ($Q_{neat} > Q_{nano}$). Since the solvent (i.e. water) is unique, flow rate is proportional to mass flow rate. So, a higher amount of solvent is absorbed by the neat sample.

4. Conclusion

Five different gel coats were prepared using epoxyvinylester resin, neopentylglycol unsaturated polyester resin and their 75/25, 50/50 and 25/75 blends. The water absorption properties of gel coats were improved with the addition of nanographene. The results showed that unsaturated polyester resin gel coat had the highest and epoxyvinylester resin gel coat had the lowest water absorption levels. The water absorption of blends obeyed the mixture rule, so the increase of polyester resin content in the blend resulted in an increase in water absorption. Also, in the first part of the water absorption curves corresponding to the blends, water absorption reduction are considerable compared to the calculated values. This can be due to, covered the vinylester polar groups in the blends by neopentyleglycol hunging group in polyester resin.

References

[1] Abdullah H, Al Araimi S, Siddiqui RA. The effects of weathering on mechanical properties of glass fiber reinforced plastics (GRP) materials. IIUM Engineering Journal. 2000;1(2)..

[2] ASTM A. D570 Standard Test Method for Water Absorption of Plastics. ASTM D792 Standard Test Methods for Density and Specific Gravity (relative density) of Plastics by Displacement. ASTM D. 1990;2240.

[3] Bora C, Bharali P, Baglari S, Dolui SK, Konwar BK. Strong and conductive reduced graphene oxide/polyester resin composite films with improved mechanical strength, thermal stability and its antibacterial activity. Composites Science and Technology. 2013 Oct 18;87:1-7..

[4] Bora C, Gogoi P, Baglari S, Dolui SK. Preparation of polyester resin/graphene oxide nanocomposite with improved mechanical strength. Journal of Applied Polymer Science. 2013 Sep 15;129(6):3432-8..

[5] Tsuzuki EK, Taniguchi C, Filho AC. Gelcoat Blistering And the Use of Glassflakes. InISOPE International Ocean and Polar Engineering Conference 2002 May 26 (pp. ISOPE-I). ISOPE..

[6] Elkamel A, Alhumade H, Omidbakhsh N, Nowruzi K, Duever T. Chemical Product Formulation Design and Optimization: Methods, Techniques, and Case Studies. John Wiley & Sons; 2023 Jan 17..

[7] Armorcote IM. Weathering the heights with gel-coat. Reinf. Plast. 1993 Jan;37:46-8..

[8] Jawahar P, Balasubramanian M. Preparation and properties of polyester-based nanocomposite gel coat system. Journal of Nanomaterials. 2006 Jan 1;2006..

[9] Kim YH, Park JM, Yoon SW, Lee JW, Jung MK, Murakami RI. The effect of moisture absorption and gel-coating process on the mechanical properties of the basalt fiber reinforced composite. International Journal of Ocean System Engineering. 2011;1(3):148-54.

poval.“http://www.poval.jp/english/poval/tec_info/ti_02.html n.d.” 2010.

[10] Crump S. A study of blister formation in gel coated laminates. Marine Applications of Composite Materials. 1986.

[11] Sabzi M, Jiang L, Liu F, Ghasemi I, Atai M. Graphene nanoplatelets as poly (lactic acid) modifier: linear rheological behavior and electrical conductivity. Journal of materials chemistry A. 2013;1(28):8253-61..

[12] See SC, Zhang ZY, Richardson MO. A study of water absorption characteristics of a novel nano-gelcoat for marine application. Progress in Organic Coatings. 2009 Jun 1;65(2):169-74..

[13] Shah AP. Moisture diffusion through vinyl ester/clay nanocomposites. West Virginia University; 2001.

specialchem4coatings.“http://www.specialchem4coatings.com/tds/xgnp-graphene-nanoplatelets-grade-m/xg-sciences/38113/index.aspx n.d.” 2009.

[14] Swain S. Synthesis and characterization of graphene based unsaturated polyester resin composites. Transactions on electrical and electronic materials. 2013 Apr 25;14(2):53-8..

[15] Zhang ZY, See SC, Richardson MO. Characterisation and evaluation of nano gelcoat degradations in marine environment. Journal of nanoscience and nanotechnology. 2009 Jun 1;9(6):3355-63..

Zhao, H. LRKY. “composites: Part A.” 2008: 602-611.