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DEGRADATION OF GFRP MARINE LAMINATES WITH NANO PARTICLE MODIFIED COATINGS

ABSTRACT

Water absorption and surface blistering behaviour was studied for polyester-matrix laminates with SiO_2 nanoparticle reinforced gel coats. Accelerated water immersion tests at 37°C showed that addition of 10% nanoparticles increases blisters incubation time by ca. 50% compared to 5% and 0% nanoparticles composites.

Keywords: *Polymer composites, nano composite, durability, scanning electron microscopy (SEM)*

INTRODUCTION

Degradation of the surface layers of glass fibre reinforced /polymer boats is a problem to the boat building industry and their suppliers. World leading producers of resins and gel coats are offering new materials in order to reduce water immersion effects [1]. Recently nano-particles have been proposed as a filler of the coating systems [2]. Resins filled with ceramic nano-particles are expected to offer: significantly improved scratch and abrasion resistance, no reduction in transparency and gloss for the coating, barrier effect against gases, water vapor and solvents, increased weathering resistance and inhibited thermal aging, reduced thermal expansion and internal stresses , increased tear resistance, fracture toughness and modulus improved adhesion to a large number of inorganic substrates (e.g. glass, aluminium), no adverse impact to numerous desired properties such as curing speed and prevention from sagging , improvement to other desired properties such as: thermal stability, stain-resistance, heat conductivity, dielectric properties.

Degradation of polymer composite laminates involves water absorption effects such as surface blistering and microstructure degradation, which results in impairment of mechanical performance of the construction. Water absorption behaviour of polymer nanocomposites was discussed primarily for polymers reinforced with nano-clay [3,4], as well as for inorganic nanoparticles [5,6]. The rate of water absorption in polyamide 6-clay nanocomposite was reduced by 40%, compared with the pure polymer [7]. There are contradictory reports of water absorption for epoxy- clay nano composites. No, or very little, decrease in water absorption due to the addition of nano-clay was reported, only the rate of water absorption was reduced. The programme of research on the development of mixing technique for epoxy-clay nanocomposites resulted in an increase of fracture toughness and a reduction of water uptake in these materials. It was found that, upon incorporating organoclay into the epoxy, maximum water uptake and diffusivity decreased with increasing clay loading. Diffusivity decreased, e.g. by about 20% for 7,5-phr clay loading, with the reduction strongly depending on the dispersion quality [3]. Almari at al [4] obtained an improvement in water absorption behaviour of epoxy filled with various nanoparticles. The maximum water absorption found for 0%, 1,5%, 3% and 5% nanoclay composites was: 2,34%, 2% 1,9% 1,76%, respectively. Similar reduction was obtained for HNT (halloysite nanotubes nanofiller) and for n-SiC. In the latter composite, the maximum water absorption found for 0%, 1,5%, 3% and 5% n-SiC was: 2,34; 1,83%, 1,67%, 1,56%, respectively. The substantial decrease of permeability, brought about by the nanocomposite structures, was attributed to the tortuous path presented by high aspect ratio clay [5].

It appears thus that the scientific and technical data reported so far do not allow generalizations regarding the effect of nano particles on the water immersion behaviour of polymer composites. Accordingly further extensive studies, including of blistering behaviour, are needed for new materials. The aim of the present work was to assess the water immersion behaviour and microstructure degradation of typical marine glass fibre reinforced laminates with some SiO_2 nanoparticle reinforced gelcoat.

MATERIALS AND EXPERIMENTS

Typical marine glass fibre-reinforced polymer (GFRP) laminates were investigated in this study. The surface of the specimens was coated with isophtalic gelcoat: pure (0%Nano) or mixed with SiO_2 nano-particles 5wt % (5%N) or 10wt% (10%N), The laminates were fabricated using vacuum bagging method.

The laminate plates were cut into specimens 45 x 45 mm. The sides of the specimens were protected by the matrix resin to prevent fast water sorption through the edges.

Water sorption and blistering behaviour were tested in a stainless steel container with temperature control system. Specimens were placed on a wooden frame with a plastic grid which was floating on the surface of water inside the container similar to the boat immersed in water. Accelerated tests were made at 37°C for ca. 40 days. The mass of the specimens was evaluated using a 0,1mg precision scales (*RADWAG WPA 180/C/1*). Weight gain was plotted as a function of square root of time (days). Blistering behaviour of the specimens was examined by observation of the blister incubation time and monitoring of blisters evolution.

In order to observe the evolution of microstructural damage corresponding to blisters formed on the surface of the gel coat layer the damaged specimens were cut across the blisters and the cross sections were ground using emery paper 600, 1000 and 1500, polished using 3μm alumina powder and examined using scanning electron microscope Philips FEI XL 30 ESEM**.**

RESULTS AND DISCUSSION

Fig. 1 illustrates water absorption behaviour at 37°C. Arrows point to the blister incubation times (Table 1). It is clear that addition of nanoparticloes extends the blisters incubation time, however at 5%N the effect is insignificant. 10% N offers ca. 50% improvement compared to 0%N and 5%N. To be noted is rapid increase in water absorption rate (which normally tends to stabilize at longer ageing times) when first blisters appear. This is due to the beginning of irreversible damage which accelerates water sorption. The difference in surface blistering behaviour is noted in Fig. 1b.

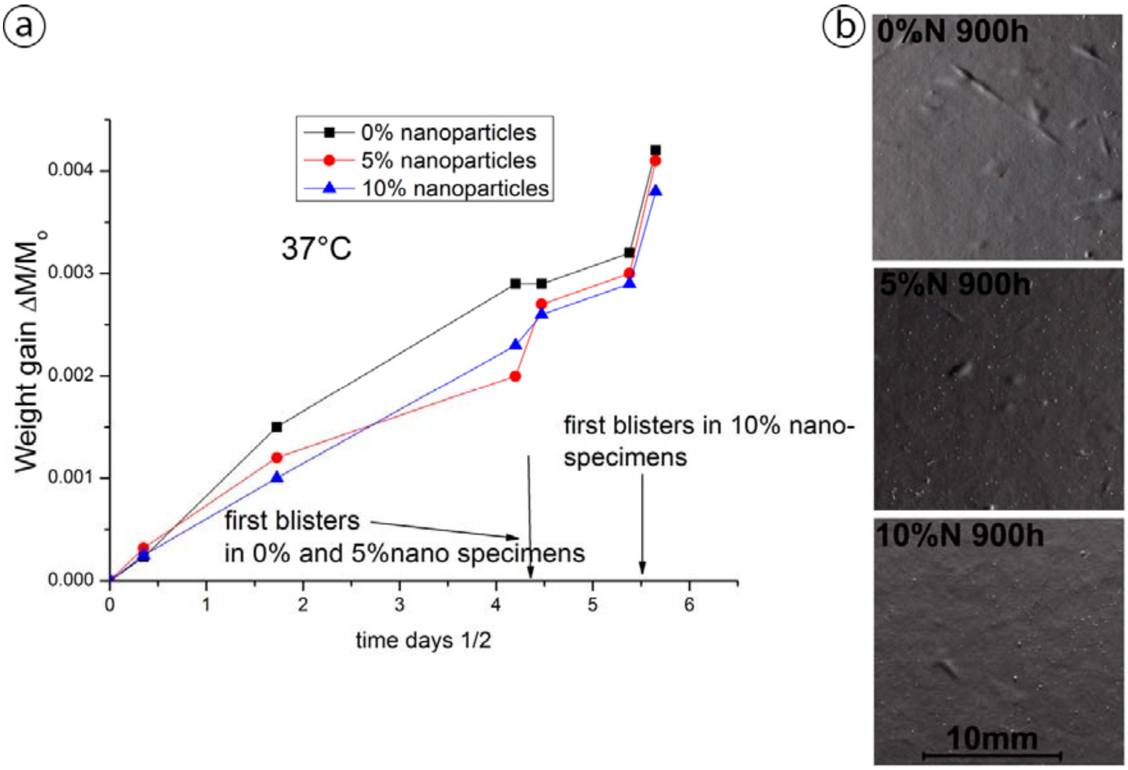

Fig. 1. Water absorption (a) and blistering behaviour (b-d) of the specimens with nanoparticle reinforced gel coat at 37°C after 900 hours ageing: b) 0%N, c) 5%N, d)10%N

Table 1. *Blister incubation times for nanocoatings at 37°C*

	37°C		
	0%	5%	10%
Blisters incubation time [days]	18	20	32

Microstructures

Fig. 2 illustrates damage type corresponding to 0% and 10% nanoparticles after 900 hours exposure in water at 37°C. To be noted are: a subsurface gel coat crack in 10% N and a complex crack involving gel coat crack combined with fibre/matrix interface crack in 0%N specimen. In composites with dense nanoparticle network the tortuous water molecules diffusion paths prevent early water ingress and local internal pressure buildup which results in delayed blistering and laminate degradation.

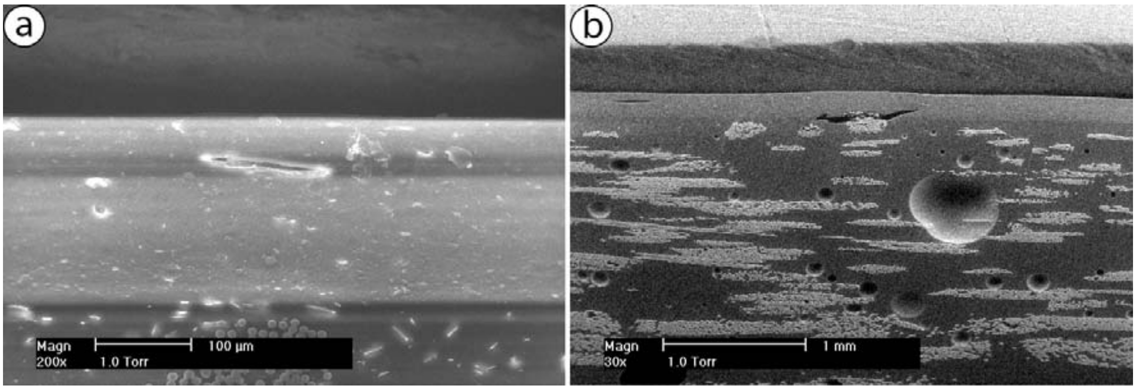

Fig. 3. Damage corresponding to 0% and 10% nanoparticles after 1000 hours exposure in water at 37°C

CONCLUSIONS

Water absorption and surface blistering behaviour was studied for polyester -matrix laminates with SiO_2 nanoparticle reinforced gel coats. The main conclusion is that the addition of 10% nanoparticles increases blisters incubation time by ca. 50% compared to 5% and 0% nanoparticles composites, accordingly such materials can be recommended for further studies.

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