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Effect of nanoclays on the mechanical properties and durability of novolac phenolic resin/woven glass fiber composite at various chemical environments

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ABSTRACT

Both natural montmorilonite (CN) and organically modified montmorilonite (CB) improved significantly the mechanical performance of novolac phenolic resin (PF)/woven glass-fiber (GF) composites due to their nanodispersion and good interfacial interaction with the matrix. It was revealed that the incorporation of 2.5 wt% of the clays enhances the elastic modulus up to 38% for CN and 43% for CB. Aging of PF/GF composites at various aqueous solutions, i.e. water, brine and acidic environments, increased stiffness of the composite (~100–250% increase in elastic modulus) due to possible secondary crosslinking caused by water molecules and hydroxyl groups of PF resin. However, aging led to the reduction of strength caused by the matrix degradation due to hydrolysis and interfacial debonding. It was found that both clays diminished durability of PF/GF composites probably due to their hydrophilic nature enhancing water absorption.

1. Introduction

Glass-fiber reinforced plastic (GRP) consisting of continuous glass-fiber and polymer matrix is a class of fiber reinforced polymer composites (FRPC) which is increasingly being employed in a wide variety of structural applications ranging from general purpose parts in construction and civil infrastructures to high performance structural components in aerospace and aircraft industries. GRPs are promising alternatives for many applications where conventional materials like steel, aluminum and ceramics have already been used. Such a worldwide growing attention for GRP is originated from its low cost-to-performance, high internal damping, high strength-to-weight ratio, high modulus-to-weight ratio, superior corrosion resistance and easy processing compared to conventional materials.

Despite the unique performance of GRP, it undergoes a significant degradation upon exposure to wet and chemical environments which always leads to considerable loss in mechanical performance and durability [1]. Therefore, when the GRPs are intended to be used in environmental conditions, their long term durability and aging behaviors would be prime concern. Many attempts have been made to obtain deep insight into the mechanisms of environmental degradations over many years [1]. It is known that the moisture/chemicals adsorbed by GRP can promote the degradation of polymer/fiber interfacial interaction [2], polymer matrix [3] and may also lead to significant blister resulting in catastrophic deterioration of GRPs [4].

It is well known that the water, whether by itself or in combination with other chemicals, is major source of degradation in polymer matrix and polymer/glass-fiber interface at room temperature which can deteriorate the GRP through different mechanisms. It may cause some irreversible degradation like hydrolysis of matrix and interface, matrix microcracking, secondary crosslinking of matrix and/or reversible changes such as plasticization and swelling of matrix [5]. These degradation mechanisms are primarily dominated by the polymer matrix type and the nature of fiber surface sizing, even though exposure time and conditions can also affect them sensibly [6]. Consequently, GRP with a particular polymer matrix certainly exhibits specific durability behavior.

The epoxy, unsaturated polyester and vinylester resins are the most widely used polymer matrices in GRP for structural applications. However, GRP based on phenol formaldehyde (PF), so called phenolic, resin has also received considerable attention in some applications such as aerospace, automotive, sport and marine [7–9]. This is due to the fact that the PF resin is a low-cost and easily processable resin with a numerous interesting properties such as high resistance against chemical environment, excellent

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fire performance and superior thermal insulation characteristics. Phenolic resin is commercially available in two different forms including resole and novolac whose difference is in the phenol/formaldehyde ratio as well as polymerization reaction environment, i.e. acidic or basic conditions [10], during synthesizing.

By emerging nanotechnology, the attempts have been made to improve the performance of polymeric materials essentially by incorporating a few percent nanoparticles, i.e. less than 5 wt%. Amongst the nanoparticles used in nanocomposites, nanoclays or silicate layers have been much considered in polymer nanocomposites. This is due to the fact that nanoclay is an inexpensive natural mineral with a large aspect ratio, i.e. 100–1000, along with high mechanical and thermal properties. The large aspect ratio offers a unique opportunity to get high barrier properties against the diffusion of gaseous and liquid materials through the formation of tortuous path in the corresponding nanocomposites [11]. This has made polymer/clay nanocomposite a promising candidate in many applications where high barrier properties along with high mechanical performance are highly required, like food packaging.

In the past decade, the attempts have been made to examine the role of nanoclay in the improvement of GRPs. In such ternary hybrids, the nanoclay may be present within polymer matrix and/or on the polymer/glass-fiber interface depending on the thermodynamic affinity between the polymer and fiber surface with clays [12,13]. This can provide distinctive opportunities to get multifunctional composites with combined properties of glass-fiber and nanoclay. However, the uniform and nanoscale dispersion of clay and its interaction with polymer matrix as well as the glass-fiber are the major concern in these ternary nanocomposites.

The literature has shown that GRP nanocomposites based on epoxy and unsaturated polyester resins have been mostly investigated [14–24]. It is shown that nanoclay is able to improve the mechanical properties of GRP, especially its stiffness, considerably. Kornmann et al. [22] obtained glass fiber/epoxy-layered silicate nanocomposites laminates and observed an improvement in the flexural modulus (6% increment) and strength (27% increment) with the addition of clay. Subramaniyan and Sun [25] showed that addition of nanoclay increased the compressive strength of glass fiber reinforced composites. Mohd and Zulfli [26] studied the incorporation of silane-treated clay loading on the flexural properties of epoxy/glass-fiber composites and reported 13% increment in flexural modulus. Kabakov et al. [27] also concluded that the nanoclay makes the material stiffer when compare to the base material. However, it is unanimously agreed that the enhancement of mechanical properties is directly limited to its exfoliation and interfacial interaction with resin matrix and fiber.

It was also reported that the nanoclay can reduce the equilibrium water uptake and diffusivity of thermosetting matrices significantly [15]. This behavior may lead one to assume that the nanoclay would be able to improve the environmental aging and long term durability of GRP. However, the literature exploring the role of nanoclay on the durability of GRP at environmental conditions is very sparse for epoxy and unsaturated polyester resin [15]. To the best knowledge of the authors, there is no information in open literature on the durability analysis of the phenolic resin based GRP and its nanocomposites with nanoclay. As the phenolic resin is hydrophilic molecules with large amount of hydroxyl groups, it can be susceptible to absorb water molecules. Therefore, the degradation mechanisms of such composites and nanocomposites in aqueous solution would be interesting and have practical importance.

The objective of this research was to examine the role of nanoclays on the mechanical and morphological characteristics of GRP composites based on novolac phenol–formaldehyde, named here PF/GF. Additionally, the role of clay on the durability of PF/GF composite under various conditions was also investigated. Since there are no well-documented data on degradation of these composites under various environmental conditions, the aging behavior was analyzed in several aqueous solutions including distilled water, brine, acidic and alkaline in order to obtain deep insight into the degradation mechanisms of PF/GF/clay nanocomposites.

2. Experimental

2.1. Material

E-glass fabrics, phenolic thermosetting resin and two types of montmorillonite clay particles were used to fabricate composite laminates. The polymeric matrix was a novolac type PF (Novolac IP502, hexamethylenetetramine content 10 wt% and density of 1.28 g/cm^3) obtained from Rezitan (Tehran, Iran). Natural montmorillonite (cloisite Na^+, d_{001} = 11.7 Å) and organically modified with a quaternary ammonium salt, MT2EtOH (cloisite 30B, modifier concentration = 90 meq/100 g clay, d_{001} = 18.5 Å), were purchased from Southern Clay Products (Austin, TX). Plain weave E-type glass fiber (code: CYS-EWR, surface density of 200 g/m^2) was provided by Chengdu Chang Yuan Shun Co. (china).

2.2. Preparation of prepregs

Layered clay/phenolic nanocomposite resin systems were first prepared with 0.5, 1.5 and 2.5 wt%, based on resin weight, of Cloisite Na^+ (CN) and Cloisite 30B (CB). To do this, the clay and phenolic resin were dispersed homogeneously in methanol (from Merck) at room temperature and mechanically stirred for 90 min to promote the dispersion [28]. Then, the suspension was hold in an ultrasonic bath for 30 min in order to enhance nanodispersion of the clay platelet within the resin. The phenolic/clay solution was used to impregnate the glass fabric using the solvent impregnation method. After suspending for 2 days at the room temperature with natural condition, the impregnated fabrics were pre-cured at 135 °C in an oven for 3.5 min to obtain B-staged prepregs.

2.3. Composite fabrication

Seven layers of prepregs with a plain dimension of 150 mm × 100 mm were stacked together inside the mold and then compression molded under the pressure of 50 bars and at 150 °C for 30 min with degassing during the molding. A post curing cycle (6 h at 150 °C, 2 h at 160 °C and 3 h at 180 °C) was applied in an oven following in mold curing stage. Fiber weight percent of the composites was determined by matrix burn-off method, described in ASTM D5284, and measured to be about 60–63 wt% (in proportion to volume percent of 51–53%)for all laminates.

2.4. Aging conditions

In order to study the effect of environments, samples with dimension of 100 mm × 15 mm × 1 mm were immersed in 4 different aqueous solution including distilled water, brine (30 g/100 cc NaCl solution), acidic (1 M HCl) and alkaline (3 M NaOH). These media were chosen harsh to possibly impart greater damage to the samples in a shorter time. All solutions maintained at room temperature up to 75 days. After immersion, samples were taken out and dried at 70 °C in vacuum pressure of 80 mm Hg for 12 h to remove moisture and provide proper samples for testing.

2.5. Characterization

The structure of the nanocomposites was studied using X-ray diffraction (XRD). A Philips PW3050 diffractometer was used to