



## Durability study of vinyl ester/silicate nanocomposites for civil engineering applications



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### ABSTRACT

The durability of fiber-reinforced polymer (FRP) composite materials in humid and harsh environments is an important consideration for acceptance of these materials in civil engineering applications. Reducing the moisture ingress may improve the durability of FRPs. The addition of modified inorganic powder, such as silicate nanoparticles, may improve several important properties of polymers, such as barrier properties, fire retardancy, dimensional stability and mechanical strength. The present work aims to evaluate the effect(s) of the addition of silicate nanoparticles on the durability-related properties of vinyl ester polymer used as matrix for FRPs in civil engineering applications. To conduct this preliminary study, nanocomposites containing 5% organo-modified or untreated silicate were characterized by using X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). The diffusivity of moisture was measured by immersing samples in a 50 °C water bath. Barrier properties were determined by measuring the maximum water uptake, water absorption rate and coefficient of diffusion. Aging was performed by complete immersion of nanocomposites samples in a NaOH solution at 50 °C. Scanning Electron Microscopy (SEM), tensile tests and Fourier Transform Infrared spectroscopy (FTIR) analyses were performed before and after conditioning to evaluate the matrix degradation. Experimental results show that the use of organo-silicate leads to an improvement of barrier properties characterized by a decrease of the coefficient of diffusion. It also increases mechanical properties and leads to a significant decrease of chemical degradation.

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### 1. Introduction

Polymer nanocomposites (PNC) are multiphase solid materials containing a component with one, two or three dimensions of less than 100 nm dispersed in a thermoset or thermoplastic matrix [1]. This new family of materials has drawn great attention from scientific community because of their high thermal [2], mechanical [3] and barrier properties [4]. Nowadays, the use of nanocomposites increases in many industrial sectors, such as automotive, marine transportation, sports and leisure or civil engineering [5]. In this sector, polymer nanocomposites can be used in structural restoration and rehabilitation of existing damaged structures [6]. Moreover, the inert character of several polymer matrixes makes PNC very good anticorrosive materials [7] which can be used as protective surface coating. The improvement of knowledge in

nanotechnologies leads to the development of new cost-effective and more performing polymer nanocomposites material [8].

There are three categories of nanocomposites, according to the type of filler: (1) Spherical or three-dimensional nanoparticles, such as silica fume, which is extensively used in PNC [9]; (2) Two-dimensional nanoparticles such as carbon nanotubes, nanowires or crystalline whiskers, which provide outstanding mechanical and thermal properties [10,11]; and, (3) One-dimensional nanoparticles constituted of stacks of 1 nm thick platelets. Because of their nanometric thickness, the one-dimensional fillers such as phyllosilicates, offer a very large specific surface area, which magnifies the interaction with the resin chains and therefore leads to a significant improvement of the resin properties such as diffusion barrier or mechanical properties [12]. Phyllosilicates are constituted of stacks of tetrahedral  $\text{Si}_2\text{O}_5$  layers between alumina or magnesia octahedral layers [13] (Fig. 1). Among them, montmorillonite [14], mica [15], hectorite [16] and many other smectite-type clays have been studied as reinforcement in polymer, especially for gas permeability applications [17]. Previous study has shown that the

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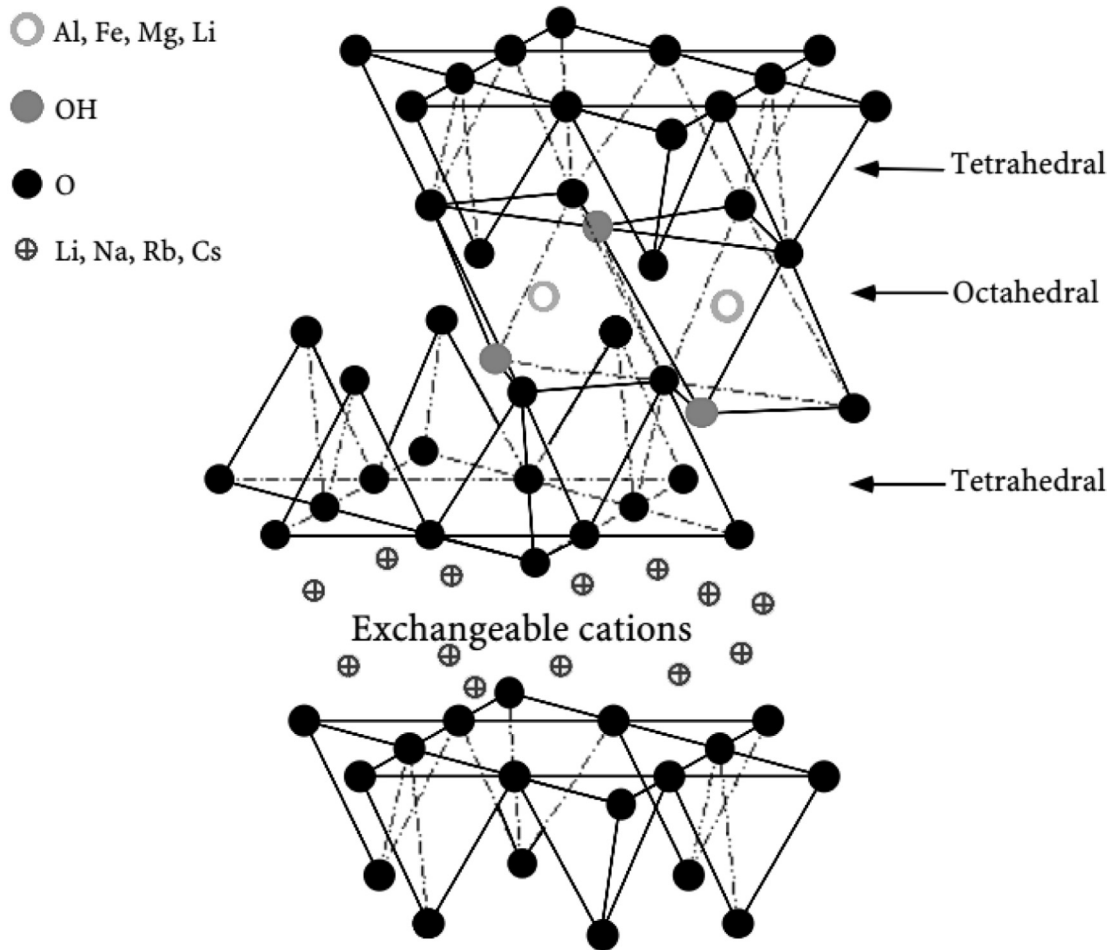


Fig. 1. Characteristic structure of 2:1 layered silicates [42].

mechanical properties of thermoset polymer are improved by adding up to 5 wt% of nanoclay. Above 5 wt%, properties decreased because the mixture itself became too viscous, thereby forming pores during the polymerization process [18].

One of the most interesting properties of silicates is their high capacity to exchange cations, which allow the substitution of small cations, such as sodium ion, by organic salts [19]. The grafting of large hydrophobic organic molecules between silicate platelets increases the basal spacing, i.e. the spacing between two platelets. Therefore, it improves their affinity with the polymeric chains, which can diffuse between these platelets and consequently enhances their dispersion [20].

A previous study has shown that grafting of octadecylammonium (ODA), C18 carbon chain terminated by an ammonium group, at the surface of nanosilicate seems to be the most promising way to intercalate layered silicate [19].

Depending on the degree of dispersion in the polymeric matrix, three types of polymer composites can be obtained (Fig. 2): i) Conventional composite or micro/macro-composite in which the basal spacing is too small to allow polymer chains to diffuse between the platelets [21], ii) Intercalated nanocomposite in which the polymers chains diffuse between platelets and increase the interlayer basal spacing without separating the platelets [22], and, iii) Exfoliated nanocomposite. In the case of exfoliated nanocomposites, the stacked structure is destroyed and platelets are no longer bonded together. Exfoliated structure is the optimized

layered nanocomposite because the specific area of the silicate platelets is extensively increased leading to more interactions between platelets and polymer matrix. Therefore, several properties of the composite are greatly enhanced such as stiffness, glass transition temperature and storage modulus [23,24].

Epoxy polymers and their derivatives are essentially used for molding micro- and nanocomposite materials [25,26]. Many studies have been conducted on different nanoclay/epoxy systems with successful intercalation or exfoliation [27] whereas polyester or vinylester-based thermoset resins, generally used in civil engineering applications, did not receive the same attention. Epoxys are thermoset resins with very high mechanical and thermal properties as a result of their very dense network [28]. Vinylesters (VE) are epoxy-type polymers with a methacrylate termination and provide slightly lower thermal and mechanical properties than epoxy [29]. However, VE are widely used in civil engineering because of their low ester content and the presence of protecting organic groups, such as methyls or phenyls, which provides a higher chemical resistance than any other thermoset [30]. Apart from being used as mechanical reinforcement and barrier materials, nanoclays may be used for improving durability performance of composites. Coupled with a corrosion resistant matrix, such as VE, these materials would offer great resistance against hydrothermal aging. Most of the durability studies are focused on epoxy systems [31] while vinylester systems, which are more resistant to corrosion, do not benefit from the same attention.

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