Progress in Organic Coatings 77 (2014) 124–130

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Morphology, rheological and protective properties of epoxy/nano-glassflake systems

Mehdi Ghaffari[a,*], Morteza Ehsani[b,**], Hossein Ali Khonakdar[b]

[a] Department of Polymer, Golestan University, P.O. Box 155, Gorgan, Golestan, Iran
[b] Iran Polymer and Petrochemical Institute, P.O. Box 14965-115, Tehran, Iran

ARTICLE INFO

Article history:
Received 27 December 2012
Received in revised form 24 April 2013
Accepted 29 August 2013
Available online 24 September 2013

Keywords:
Nano-glassflake
Rheological properties
Morphology
Protective coatings
Nanocomposite

ABSTRACT

The effect of the glassflake nanoparticles on the rheology, morphology and protective properties of epoxy/glassflake nanocomposites has been studied in this work. Mechanical mixing and sonication process were used to incorporate nano-glassflakes (NGF) into the epoxy. Effects of the time and method of mixing on the morphology and dispersion quality of NGF/epoxy were studied by means of scanning electron microscopic (SEM). Results showed that a 30 min mechanical mixing followed by a 30 min sonication is a best mixing process to design nano-scale glassflake composites. The rheological analysis of epoxy pre-polymer/NGF dispersions indicates that an addition of NGF up to 1 wt% forms microstructure and improves the rheological properties. Barrier properties of the epoxy/NGF coated samples were evaluated by electrochemical impedance spectroscopy (EIS) as a function of immersion time in a sodium chloride solution (5 wt%). The experimental results showed that the barrier properties of the epoxy/NGF coating systems improved by an increase of the NGF content up to 0.5 wt%.

1. Introduction

Due to the high toxicity associated with inhibitive pigments such as strontium or zinc chromates, various studies have been carried out to develop environmentally acceptable coatings [1]. Recently, epoxy coatings with inorganic nanofillers have been studied for an improved coating protective performance [2].

The incorporation of glassflakes into coatings and plastics provides significant performance advantages compared with many other forms of reinforcement. Consequently, an increasing use of glassflake reinforced materials for high performance engineering and commodity products is experienced. The improvement of the properties includes a decrease of the warpage reduction and shrinkage as well as an increase of dimensional stability, surface hardness wear resistance, tensile and flexural stiffness. Glassflake reinforced products also exhibit a relatively high resistance to weathering and chemical attack [3,4].

The ultimate properties of nanocomposites are strongly dependent on the particle size, degree of dispersion, and the interactions occurred between the interface of particles and polymer matrix [5–7]. As the dimension of inorganic additives reduced to nanoscale size, a homogeneous dispersion of inorganic parts in the organic matrix dramatically become feasible [8,9], owing to the lack of affinity between the interfacial contact area of inorganic fillers and organic polymers. Therefore, a proper remedial measure for this flaw is crucial to develop new nanocomposites. Rheological measurement is one of the most effective methods to analyze nanocomposites [10–13]. The rheological percolation has been correlated to the electrical percolation in the CNTs/polystyrene PNCs [14,15], mechanical properties of copper nanowire/polystyrene PNCs [16,17], and microwave properties in acrylic, polyurethane, and epoxy composites [18]. Up to now, most of the reports focus on the study of thermoplastic nanocomposite [19–26] and a few studies reported the thermosetting nanocomposite properties [27,28]. No relation between rheological properties and barrier protective of nanocomposite coatings has been reported.

Recently some researches have been conducted on epoxy/glassflake systems. The effect of NGF on curing kinetic of epoxy/polyaminoamide system was investigated in our previous work [29,30]. It was found that the presence of NGF reduced the activation energy of curing reaction. A comparison of the effect of NGF and montmorillonite organoclay (OMMT) on corrosion performance of epoxy coating has been conducted by Nematollahi and et al. [31]. The results indicated that NGF filled specimens display a better corrosion performance than that of OMMT filled ones. Moreover, Souto et al. investigated the barrier properties of epoxy/polyaminoamide/glassflake system on to different substrates [32]. It was found that this coating is more strongly adhered

* Corresponding author at: Department of Polymer, Golestan University, P.O. Box 155, Gorgan, Golestan, Iran. Tel.: +98 171 4430518; fax: +98 171 4430518.
** Co-corresponding author.
E-mail addresses: m.ghaffari@gu.ac.ir (M. Ghaffari), m.ehsani@ippi.ac.ir (M. Ehsani).

0300-9440/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.porgcoat.2013.08.014

and exhibits better protection characteristics when applied onto carbon steel substrates compared to galvanized steel.

In this paper, we report on our attempts to understand the link between the dispersion of nano-glassflake in an epoxy resin and the resulting protective properties. Effects of mixing time and method on dispersion morphology of NGF in epoxy are analyzed by SEM and EDX to achieve the optimum mixing process procedure. Then, the epoxy nanocomposites including 0.25–2% NGF are prepared and the rheological behaviors of the epoxy/NGF nanocomposites such as viscosity, storage modulus, and loss modulus are investigated. The effect of NGF on corrosion protective performance of epoxy coatings are also studied by means of electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Materials

The epoxy resin used in this study, Epikote1001-X-75, was supplied by Hexion Specialty Chemicals Co., The Netherlands. Epikote1001-X-75 consists of diglycidyl ether of bisphenol-A (DGEBA) with an epoxide equivalent weight of 450–500 g $equiv.^{-1}$, diluted with xylene to an epoxy-xylene weight ratio of 75/25. The resin was cured with Crayamid115 supplied by Cray Valley Co., UK. Crayamid115 was a liquid polyaminoamide resin with a viscosity of 55,000 mPa s and an active hydrogen equivalent weight of 240 g $equiv.^{-1}$. Milled nano-glassflakes (NGF) with a thickness of 350 nm (GF 350 nmM) were obtained from Glassflake Ltd., UK. NGF was stored in a sealed plastic bag to prevent moisture absorption.

The samples were prepared with a dispersion of NGF in epoxy, mixed using a high speed mechanical stirrer and sonicator. Next, the equivalent amount of curing agent was added into the mixture, and mechanical mixing was continued for 3 min.

The substrate used in this work was carbon steel supplied by Q-panel Company. The samples were mechanically grinded and polished with SiC-paper (80, 120, 220, 500, 800, 1200, 4000 μm grid) in subsequence steps to obtain a mirror-like appearance. Subsequently, the samples were cleaned ultrasonically in ethanol and thoroughly rinsed for 10 s using deionized water and blown dry using compressed clean air.

2.2. Instrument

To study the morphology of NGF in epoxy, field emission scanning electron microscopy (FE-SEM) observations were performed using a Jeol JSM-7000F FE-SEM. The acceleration voltage was between 15 and 20 kV and the working distance was 10 mm.

Rheological measurements were executed using an AR 2000ex Rheometer with an environmental test chamber (TA Instrumental Company). Series of measurements were performed in cone-plate geometry with a diameter of 50 mm at 30 °C.

The impedance measurements were carried out using Autolab PGSTAT 30 at open circuit potential (OCP) in the frequency range of 30,000 Hz to 0.01 Hz with 15 mV perturbation. Working, reference and counter electrodes were coated sample, Ag/AgCl and platinum grid, respectively. The electrolyte used for the electrochemical measurements was a 5 wt% NaCl solution. The results obtained through the EIS measurements were analyzed using Z-view software.

3. Results and discussion

3.1. Morphology of nanocomposite

One of the important parts of nanocomposites preparation is dispersion of nanofiller in matrix. The morphology and final properties are completely dependent on this part of processing step. In this work, two method were used, i.e. mechanical mixing by 8 blade mixer and sonication process.

SEM and EDX were used to characterize the dispersion and alignment of the nano-glassflakes in the epoxy matrix in different mixing methods. Representative images are shown in Figs. 1–3. The SEM and EDX images in Fig. 1(a and b) shows a fractured surface for an

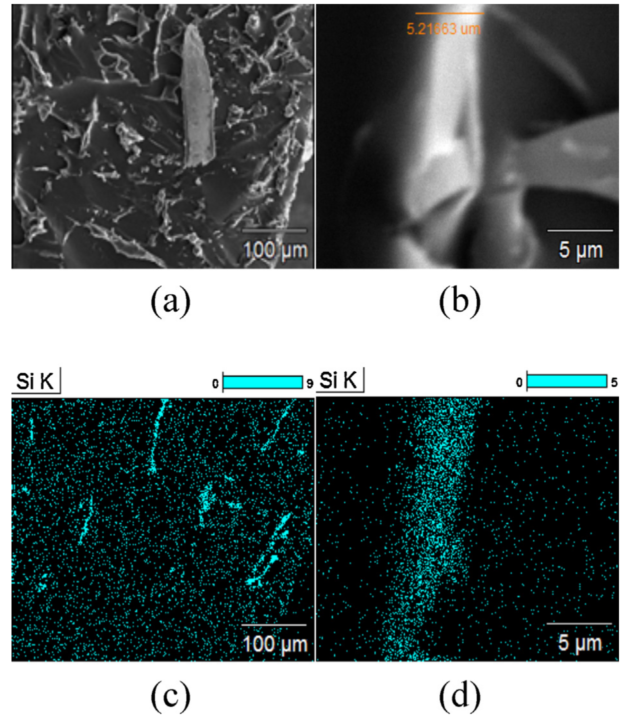

Fig. 1. SEM (a and b) and EDX (c and d) images of EPIKOTE1001/1% NGF after 30 min of mechanical mixing.

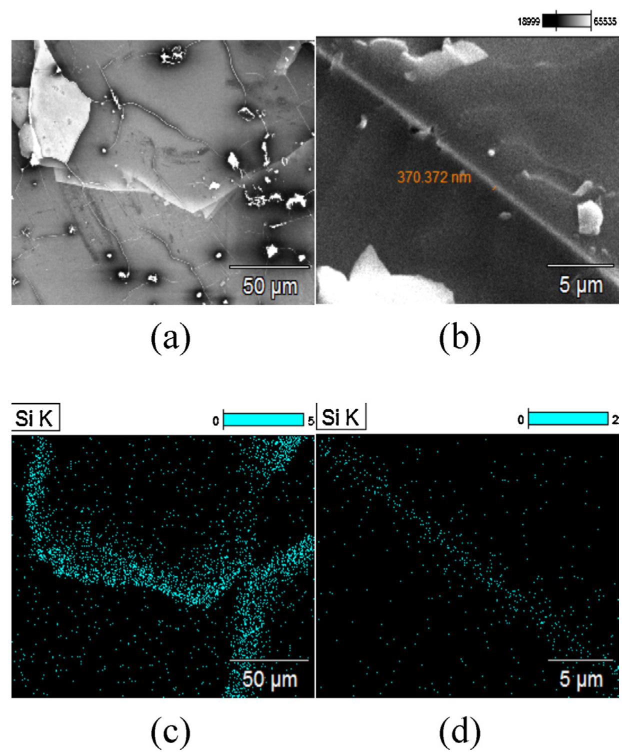

Fig. 2. SEM (a and b) and EDX (c and d) images of EPIKOTE1001/1% NGF after 30 min of mechanical mixing continued with 30 min sonication.