



Research paper

Dispersion efficiency of montmorillonites in epoxy nanocomposites using solution intercalation and direct mixing methods

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ABSTRACT

The major aims of this paper are the investigation of the effects of the mixing procedure and the montmorillonite (Mt) surface modification on the structure (optical microscopy, XRD, TEM, SEM), rheological, mechanical properties (DMA, tensile test) and corrosion stability (electrochemical impedance spectroscopy) of clay mineral/epoxy nanocomposite (CPN). Two series of CPN samples were prepared based on diglycidyl ether of bisphenol A (DGEBA) and polyamidoamine curing agent with three organophilic Mt and sodium-montmorillonite (1 wt%). Mt were mixed with DGEBA solution in the powder (direct mixing) and in the form of dispersions, preswollen in a commercial coating thinner (solution intercalation). The commercial Mt (Cloisite 30B) modified by quaternary alkylammonium ions bearing hydroxyl groups and especially Mt functionalized by primary (HDA⁺-Mt) alkylammonium ions, at loadings close to cation exchange capacity (CEC), were significantly swollen by thinner and further uniformly dispersed into CPN. Meanwhile, low gel volumes in thinner were found for more hydrophobic Mt (Cloisite 15A). The compatibility of Mt with solvents was well described by solubility and Flory-Huggins interaction parameters. In contrast to the direct incorporation of Mt powders in CPN, swelling enhanced intercalation of epoxy matrix into Mt, and for HDA⁺-Mt based CPN interlayer spacing reached 4.4 nm. The usage of HDA⁺-Mt organoclay and solution intercalation procedure provided the highest enhancement in rheological parameters (G' , G'' , η) of Mt/epoxy dispersions and glassy storage modulus, Young's modulus and barrier properties of cured CPN.

1. Introduction

The clay mineral/polymer nanocomposites (CPN) filled with low loadings (< 5 wt%) of clay minerals have attracted large interest from the coating industry thanks to the significantly enhanced corrosion stability (Nematollahi et al., 2010; Piazza et al., 2011), barrier (Osman et al., 2004; Yeh et al., 2006), mechanical (Basara et al., 2005; Liu et al., 2004, 2005; Yasmin et al., 2006) and thermal properties (Lakshmi et al., 2008; Wang et al., 2008), compared to microcomposites. The unique properties of novel CPN materials originating from the large specific surface area of clay minerals, once dispersed at a nanometric level within polymer matrix, have been achieved.

Montmorillonite (Mt), belonging to the structural family of 2:1 smectite clay minerals, has been frequently applied in CPN because of its abundance and high cation exchange capacity. The Mt particles are composed of 1 nm thick hydrophilic layers with lateral dimensions of 0.5–1.0 μm . In the dry state, layers are organized into lamellar

structures called tactoids via van der Waals forces, and further aggregated in micro-sized agglomerates. The high surface energy of the layers restricts their uniform dispersion (exfoliation) in a hydrophobic polymer matrix. The functionalization of Mt surface, through ion exchange with modifiers in the interlayer space, increases compatibility between polymer and nanofiller and enables diffusion of polymer molecules (intercalation). The dispersion state of organo-montmorillonites ("organoclays"), O-Mt, and interactions at the interface strongly affect the ultimate properties of nanocomposites.

Thermosetting epoxy resins are widely used in the anticorrosion coating industry due to the excellent combination of processability, mechanical properties, chemical stability, corrosion and resistance, as well as adhesiveness to the most metals. Solvent-borne epoxy coatings are applied as two-component systems that are polymerized in situ from an oligomeric epoxy precursor and a curing agent after deposition. The processing of epoxy CPN involves mixing of prepolymer and organoclays under high shear forces and curing process. Generally,

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alkylammonium ions create a favorable organophilic environment for epoxy polymer in the interlayer space of Mt (Azeez et al., 2013). Clays modified with primary and secondary ammonium ions or modifiers bearing hydroxyethyl groups were reported to be easily exfoliated in an epoxy matrix, while intercalated structures were formed with tertiary and quaternary ammonium ions (Brown et al., 2000; Lan et al., 1995; Wang and Pinnavaia, 1994). This behavior was attributed to faster epoxy polymerization rates in the interlayer space, compared to outside of the interlayer space polymerization, due to ability of acidic derivatives of Mt (i.e., exchanged with H^+ , NH_4^+ , protonated primary amines or aminocarboxylic acids) to catalyze epoxy ring opening at relatively high temperature, in the absence of a curing agent (epoxy self-polymerization), and curing reaction with diamines. Multiple reactive amino groups in modifier could be created, by using di- or tri- amines facilitated exfoliation of Mt layers (Triantafyllidis et al., 2002; Wang and Pinnavaia, 2003). The use of organic solvents in the preparation of CPN had beneficial effects on the deagglomeration of Mt and final properties of CPN (Kotsilkova, 2005; Liu et al., 2005). The lower viscosity of a solvent-based medium facilitates the movement of epoxy molecules on the Mt surface and provides homogeneous mixing at lower temperatures. Also, the stacking forces between layers are reduced when O-Mt is used in a swollen state (solution intercalation).

The swelling process of organophilic clay minerals in an organic medium represents the formation of an edge-to-edge and edge-to-face connection of stacked layers into a continuous network structures (Bhatt et al., 2013; Burgentzlé et al., 2004). It is widely accepted that the swelling process leads to delamination of clay mineral layers and is governed by the level of interactions between the exchanged surface and the solvent system. Surfactants with long alkyl chains (more than 10C atoms) and double bonds or aromatic groups in their structure favor gel formation, accompanied by expansion of the interlayer space (Hu et al., 2013; Moraru, 2001). In addition, physical properties of the chosen solvent system tailor the Mt structure in O-Mt/solvent mixtures. Burgentzlé et al. (2004) stated that in order to achieve good dispersion of Mt, the solvent must be compatible with the dual character of the organoclay, i.e. the polar character of the unmodified layer surface and dispersive character due to alkyl chains in the modifier structure. Thus, the most effective solvents were those combining polarities with a high organophilic character. Also, small quantities of solvents with polar groups (water, alcohols) alter the interactions between exchanged clay mineral surface and non-polar solvents, leading to formation of enhanced volumes of stable gels (Bhatt et al., 2013). Jordan (1949), Jordan et al., (1950) found the increased swelling of organoclays in non-polar hydrocarbons and oils when polar organic compounds (alcohol, ester, keton, anhydride) were added. Slabaugh and Hiltner (1968) and Slabaugh and Hanson (1969) studied the selective adsorption of polar components from binary liquid mixtures and measured the heat of immersion of various organophilic silicates. Dekany et al. (1975, 1978) correlated rheological properties of O-Mt suspensions in hydrocarbon–alcohol mixtures with sedimentation behavior and the selective

adsorption of the polar component. Kemnetz et al. (1989) showed that once the organoclay was well dispersed in a solvent, the addition of a polar solvent induced the immediate destruction of the gel. Although studies were conducted on the swelling of organoclays, there is a lack of reports that describe the preparation of epoxy CPN from organoclays swollen in a such a solvent mixture, as well as the correlation between swelling properties of the organoclays and structure and properties of the final CPN. Tomić et al. (2014, 2016) reported that by using thinner (xylene, *n*-butanol, methyl-ethyl-ketone) as swelling medium, improved corrosion stability, mechanical and thermal properties for epoxy CPN with 1 wt% of commercial Cloisite 30B organoclay were obtained.

Literature reports (Ho and Glinka, 2003; Ishida et al., 2000; Jang et al., 2005; Stratigaki et al., 2014; Tran et al., 2006) refer to a number of attempts to find a relationship between organoclay compatibility with solvent and polymer and the dispersion state thereof, by calculating solubility parameters and the Flory-Huggins interaction parameter.

The present paper is part of an ongoing study in which the effect of the O-Mt on the performances of epoxy CPN and their potential use in epoxy coatings are investigated. Previous studies (Tomić et al., 2014, 2016) found that CPN with 1–10 wt% nanoclay (Cloisite 30B) could be efficiently prepared by the solution intercalation method due to the thinner ability to swell the nanoclay. The aim of this paper was to investigate the impact of Mt surface modification on the structure and properties of epoxy CPN obtained by two different procedures, i.e. direct mixing and swelling of organoclays before mixing (solution intercalation). The thinner for epoxy coatings was applied as a swelling agent for two commercial O-Mt (Cloisite 30B, Cloisite 15A) as well as one prepared in the laboratory, using hexadecylammonium ions as a modifier. The efficiency of the presented methods for preparation of CPN was estimated by comparing the structure (optical microscopy, XRD, TEM, SEM), rheological and mechanical properties (DMA, tensile test) and corrosion stability (electrochemical impedance spectroscopy) of CPN with 1 wt% Mt. The extent of O-Mt dispersion in the thinner was analyzed using free swelling test. The compatibility of examined O-Mt with thinner and epoxy resin was checked using solubility parameters and Flory-Huggins interaction parameters. The insight into the relation between the O-Mt swelling behavior and the structure and properties of epoxy CPN could enable the preparation of epoxy coatings with improved protective properties.

2. Experimental part

2.1. Materials

In this study, the diglycidyl ether of bisphenol A (DGEBA) epoxy resin solution in xylene (CHS-EPOXY 210-X-75) was supplied by Spolchemie, with an epoxide equivalent weight of 445–500 g/mol (Fig. 1). The curing agent was a polyamidoamine (EPICURE 3115-X-70), supplied by Momentive, with the amine value of 69–71 mg/g. The

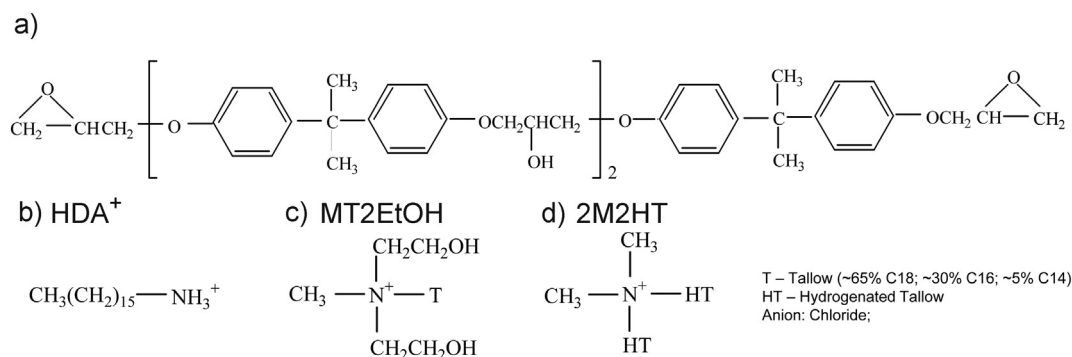


Fig. 1. The structure of DGEBA epoxy resin (a) and modifiers of organoclays HDA^+ -Mt (b), C-30B (c), C-15A (d).

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