



Rapid preparation of epoxy acrylate-clay nanocomposite: Simultaneous acrylation/nanoclay dispersion under ultrasonication

A. Dehghan*, M.J. Zohuriaan-Mehr, A. Salimi*

Dept. of Adhesive and Resin, Faculty of Polymer Processing, Iran Polymer and Petrochemical Institute, PO Box 14965-115, Tehran, Iran

ARTICLE INFO

Keywords:

Epoxy
Acrylation
Nanocomposite
Ultrasonication
UV-curing

ABSTRACT

The main theme of the present study was to prepare the epoxy acrylate-clay nanocomposite through the simultaneously acrylation reaction of epoxy resin and dispersion of clay nanoparticles under ultrasonic irradiation. The acrylation of diglycidyl ether of bisphenol-A epoxy resin was carried out through the reaction with acrylic acid in the presence of different nanoclays. In addition to UV-curing agents, two different types of commercial organoclays namely, Cloisite 15A and Cloisite 30B were used in nanocomposite films. The degree of epoxy acrylation and the UV-curing process of nanocomposite films were monitored by the corresponding absorption bands in FTIR spectroscopy. The degree of epoxy acrylation reached up to 85% for 30 min ultrasonication with a rather good degree of dispersion for both organoclays as evidenced in XRD patterns and SEM and TEM micrographs. The comparative study of different UV-cured nanocomposites films were carried out by means of different thermal and mechanical test such as DSC, TGA, DMTA and the surface hardness. The significant improvements in glass transition temperature and the thermal stability of different nanocomposites were attributed mainly to effective interactions between clay platelets and epoxy acrylate chains which result in proper dispersion of clay platelets.

1. Introduction

Epoxy resins have been commercially used in different applications in coating industry. One of the largest uses of the epoxy resins is in coatings where high chemical and corrosion resistance and adhesion are important issues. The formation of unsaturated double bonds in epoxy chain through the reaction with acrylic monomers favors epoxy resins for the UV-curing coating [1–3].

The rapid technological growth of the UV-curing technique mainly originates of its unique process characteristic which allow coating to be applied on various substrates such as plastic, wood, paper, leather, glass and even human teeth. The original driving forces behind the vast commercialization of UV-curing technology were either energy saving or solvent-free process [4–7]. The oligomers and monomers commonly used in UV-curable formulations include acrylated compounds such as epoxy acrylate [8,9], urethane acrylates [10,11], polyester and polyether acrylates [12]. The UV-curable formulations have been traditionally filled with inorganic additives to simply reduce the cost or to improve the coating functional properties [13–15].

There are several reports about the possible improvements in coating properties through using nanoparticles. Since the discovery by Toyota researchers, the organoclays could be effectively incorpo-

rated into polymer matrix. the extensive research in this area has exploded and several review articles have been published on polymer clay nanocomposites [16,17]. Compared to conventional composites, the significant enhancements in thermo-mechanical performance, barrier properties, thermal stability and even chemical resistance were observed in polymer clay nanocomposites [18–22]. However, different montmorillonite clays were organically modified to best suits for different polymeric systems. A report by Uhl showed the effect of nanoclay types on the mechanical properties of the UV-cured epoxy acrylate nanocomposite [14].

The use of different nanoparticles in UV-curing coating system resulted to commercial coatings with superior physical and mechanical properties. Due to high reactivity, low price and superior mechanical and chemical properties, The nanocomposites based on bisphenol-A type epoxy acrylates were introduced as a widely used class of acrylate resins in UV-curing systems [4]. The preparation of the clay nanocomposites based on epoxy acrylates involves two individual steps of epoxy acrylation with high efficiency in addition to effective dispersion of the nanoclays in polymeric matrix. The two individual successive steps are time and energy consuming processes. In the past few decades, it was shown that conventional heating in epoxy acrylation reaction may be replaced with the newer methods such as ultrasonic irradiation [23].

* Corresponding author.

E-mail addresses: ad_880@yahoo.com (A. Dehghan), m.zohuriaan@ippi.ac.ir (M.J. Zohuriaan-Mehr), a.salimi@ippi.ac.ir (A. Salimi).

The ultrasonic irradiation has also been widely used in different chemical fields, especially in organic synthesis and polymer chemistry. The use of ultrasound in a chemical reaction was first reported in 1920s [24]. since then it has been widely studied in different areas such as polymerization, polymer degradation [25–27], dispersion of nanoparticles [28–30] and or combination of the above fields. Besides, the ultrasound has been progressively used to realize the novel chemical reactions and to develop the reaction rate in an emerging field which is called sonochemistry. The ultrasonic cavitation creates a very extreme environment, i.e. extremely high local temperature and pressure providing the necessary heating and cooling rates for different chemical reactions [26]. Therefore, the ultrasound diminishes the reaction time and hence the energy necessary in comparison with the conventional experimental conditions with high temperature conditions for a long period of time. A comparative study on different epoxy acrylation routes was reported before by our research group [23]. To the best of knowledge, no study was conducted on simultaneous epoxy acrylation and nanoclay dispersion in polymeric matrix utilizing ultrasonic irradiation.

The main objective of this work is to introduce a rapid, reliable and facile method for the preparation of UV-curable epoxy acrylate-clay nanocomposite. The ultrasonic irradiation was utilized to simultaneously accelerate the organoclay dispersion and the epoxy acrylation reaction. Using two different organoclays, comparative experiments were conducted to study the structure-property relationship of epoxy acrylate-clay nanocomposites.

2. Experimental

2.1. Materials

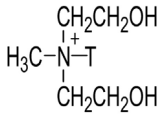
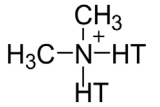
Diglycidyl ether of bisphenol-A (DGEBA)(Epikote-828)with epoxy equivalent weight; EEW = 185–192 g/mol was purchased from Momentive Co (USA). 1,6-Hexanediol diacrylate (HDDA) was obtained from Sigma-Aldrich (USA). Two organoclays namely Cloisite 15A (C15A) and Cloisite 30B (C30B) were purchased from Southern Clay Products (USA). Table 1 shows the main characteristics in addition to the chemical structure of ammonium salt of the two organoclays. The acrylic acid (AA), triphenylphosphine (TPP), hydroquinone (HQ), benzophenone, N-methyldiethanolamine (MDEA) were purchased from Merck Co (Germany) and used as received.

2.2. The preparation of the epoxy acrylate-clay nanocomposite

The DGEBA resin was added to AA at 1:1 molar ratio in the presence of TPP (1 wt.%) as catalyst and hydroquinone (300 ppm) as inhibitor.

Table 1

The properties of the two organoclay used.

Organoclay	Chemical structure of quaternary ammonium salt ^a	d-spacing (Å)
Cloisite 30B		18.5
Cloisite 15A		31.5

^a T (tallow) consisting of (~65% C18, ~30% C16 and ~5% C14) and HT (hydrogenated tallow).

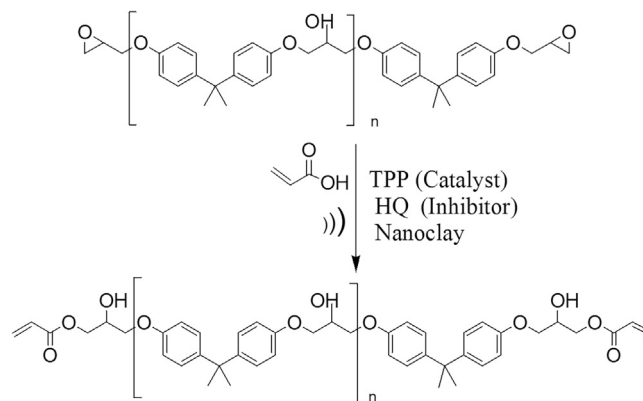


Fig. 1. Preparation of epoxy acrylate-clay nanocomposites.

The both types of organoclays were individually mixed into resin composition for 30 min. The organoclay loadings in these systems were 1, 2 and 3 wt.% based on the total resin composition. The whole synthesis was carried out in a reactor consists of a Pyrex glass tube and a titanium ultrasonic probe (KE-76) equipped with a generator Bandeling Co., HD 3200 (Germany). The ultrasonic sonicator sends ultra-high frequency pulse (20 kHz, 7 s on and 3 s off) into the mixture operating at a power of 90 W. In order to maintain constant temperature, the ultrasonic sonicator was programmed to operate continuously for 10 min, then stopped for 5 min to allow the mixture to cool down. This cycle was repeated for a total sonication time of 30 min. A schematic of the reactions in the preparation of epoxy acrylate-clay nanocomposites was shown in Fig. 1. In a sample coding system, the epoxy acrylate resin was designated as EA sample. The following number and symbol after EA refers to the weight percent and type of each organoclay used. For example, sample EA-1%C15A indicates for an epoxy acrylate resin containing 1 wt.% Cloisite 15A.

2.3. Preparation of UV-curable coating

In order to control the viscosity of the epoxy acrylate-clay nanocomposite, a maximum amount of 10 wt.% of HDDA was used as reactive diluent. The resin mixture was stirred at 100 rpm and 50 °C to obtain a homogeneous composition. The formulation was then mixed with 5 wt.% of benzophenone as a photo-initiator and 5 wt.% of MDEA as a co-initiator. The coating formulation was casted on the glassy substrate using a film applicator of approximate 90 μm wet film thickness. The coated panels were then exposed to UV radiation under a high pressure mercury lamp (1000W) for up to 8 min.

3. Characterization methods

The FTIR spectrometer (Bruker –Aquinox 55, Germany) in transmission mode from 400 to 4000 cm⁻¹ was used for tracking the changes during epoxy acrylation and UV-curing reactions.

The measurement method for the conversion of epoxy acrylation and the conversion of UV-curing reaction were defined in parts a and b, respectively.

(a) Acrylation reaction conversion

The disappearance of the epoxy group corresponding peak at 915 cm⁻¹ was used as measure of reaction progress during acrylation reaction. The aromatic C=C corresponding absorption band at 1608 cm⁻¹ was used to normalize the registered spectrums [31–33]. The conversion of reaction defines the fraction of epoxy groups that are converted to ester groups in time t and was calculated from the relative concentration of epoxy group using Eq. (1):

Download English Version:

<https://daneshyari.com/en/article/4999335>

Download Persian Version:

<https://daneshyari.com/article/4999335>

[Daneshyari.com](https://daneshyari.com)