International Journal of Adhesion & Adhesives 61 (2015) 127–136

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

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

Epoxy reinforcement with silicate particles: Rheological and adhesive properties – Part I: Characterization of composites with natural and organically modified montmorillonites

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ARTICLE INFO

Article history:
Accepted 24 May 2015
Available online 5 June 2015

Keywords:
Epoxy
Montmorillonite
Nanocomposites
Rheology
Shear-lap strength

ABSTRACT

Rheological and adhesive properties of epoxy oligomer–montmorillonite (MMT) nanocomposites containing 2 and 5 wt% of natural and organomodified clay were studied. Ultrasound treatment of epoxy–clay systems was used for their homogenization. According to rheological data, ultrasound stirring allows the development of well-dispersed systems in the case of organomodified MMT. Sonication of composites with natural clay is inefficient and leads to a poorly dispersed structure. X-ray data demonstrate increases in the interlaminar spacing for organomodified MMT (up to 2 times), which is indicative of MMT intercalation. Clay addition leads to 40–65% increase in the shear adhesion strength of the cured epoxy resin. The sonication influence on the shear adhesion strength of the system with 2 wt% of any clay is very small. Ultrasound stirring of the systems with 5 wt% of clay results in higher values of adhesion for organomodified MMT.

1. Introduction

Epoxy resins nowadays are one of the most widely used adhesives as well as polymer composite matrices because of their high mechanical and adhesion characteristics, good electric insulating properties, chemical resistance, relatively low shrinkage during curing and ease in processing [1,2]. However, epoxy resins suffer from a serious disadvantage – low impact resistance and toughness. Rubbery or thermoplastic modifiers could be used to solve this problem, and in fact, decrease in the epoxy matrix brittleness could be obtained by such modifications [3–6]. Unfortunately, incorporation of rubber modifiers into epoxy resins generally results in decrease in properties such as Young modulus, tensile strength and glass transition temperature [3,4]. Besides, when thermoplastic modifiers are used, the viscosity of the resin increases substantially. Also the price of the modifier is rather high [5,6].

Due to the factors mentioned above and motivated by recent developments in nanocomposite technology, nanofillers have been considered for epoxy resin toughening in several studies [7–17]. Different fillers have been used for epoxy resin properties enhancement: montmorillonite, natural and organically modified [7–10], silica particles [11], sepiolite [12], halloysite [13], carbon nanotubes [14,15] etc.

One of the most frequently used epoxy resin nanoreinforcements is montmorillonite (MMT) due to its availability, high specific surface area, aspect ratio and strength as well as low cost of the material [18]. MMT nanocomposites exhibit markedly improved mechanical (impact strength, toughness and even tensile strength), flame-retardant and gas-barrier properties [7–10]. However, the best enhancement of epoxy properties is obtained in the case of complete MMT exfoliation and homogenously dispersed MMT layers in the matrix [8,10,16,17]. Consequently, dispersion of the nanofiller in the matrix is considered to be the key element of nanocomposites production technology. A thorough investigation is being made regarding improvement of the MMT dispersion in different polymer matrices, achieved by different technologies, including mixing conditions variations. Surface modification of MMT by various agents is applied to facilitate interaction of the hydrophilic surfaces of MMT layers with polymers, which in turn can result in intercalation and exfoliation of the MMT layers by polymers [16,17]. As a rule, such techniques are rather laborious or environmentally unfriendly (due to solvent usage). As an alternative to traditional methods mentioned above, ultrasonic stirring was used by Wang et al. [17] to enhance the mixing effect. Ultrasound treatment resulted in a MMT interplanar

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http://dx.doi.org/10.1016/j.ijadhadh.2015.05.008
0143-7496/

distance and epoxy tensile modulus increase. Better MMT dispersion in the epoxy resin after sonication was also observed by the other researches [19–21].

So, one of the objectives of our research was to study sonication influence on both natural and organomodified MMT dispersion in epoxy resins. Rheological data were used to estimate the results of the mixing process.

It should also be mentioned that a number of papers are available, studying the influence of fillers on various properties of nanocomposites, but almost no data has been published regarding one of the most important properties of epoxy resins – adhesion. Refs. [7,22] are rare exceptions. So, another objective of our research was to study the influence of MMT on the adhesion properties of pristine polymer and to relate this data with rheological data obtained from this work and data obtained by other researchers.

Some preliminary results obtained in our work were published previously [23]. The current paper is a substantial extension to this work.

2. Experimental

2.1. Materials

Epoxy resin based on diglycidyl ether of bisphenol-A (DGEBA) from EPITAL, Russia was used. 4,4'-diaminodiphenylsulfone (DDS) from BASF, Germany was employed as curing agent. The epoxy matrix was prepared using a stoichiometric ratio of 70/30 (w/w) epoxy resin/DDS.

The following nanofillers were selected:

1. natural sodium MMT Cloisite Na^+, supplied by Southern Clay Products, USA with 12 Å interlaminar spacing;
2. Cloisite 30B-MMT, modified with quaternary ammonium, supplied by Southern Clay Products, USA (Fig. 1). According to the data, provided by the supplier, the modifier concentration was 90 meq/100 g clay, and interlaminar spacing was 18.5 Å.

Rheological measurements were made for epoxy oligomer–clay systems, containing 2 and 5 wt%, without the curing agent. The same systems with the curing agent were used to prepare samples for the shear-lap measurements. The resin/hardener ratio was as indicated above.

2.2. Preparation of epoxy–MMT compositions

2 or 5 wt% of clay was mixed intensively with epoxy oligomer at room temperature using an overhead stirrer for 5–15 min. Then the mixture was exposed to ultrasonic treatment for 2, 4 or 6 min using an ultrasonic dispergator with an immersed waveguide. A waveguide with the following characteristics was used: 1.5 cm diameter, 22.4 kHz frequency and 100 W capacity. To prepare the samples for adhesion testing the curing agent was added to the system after the ultrasonic stirring and the composition obtained was mixed at room temperature with the overhead stirrer for five minutes. The compositions were cured at 180 °C, the curing time was 6 h.

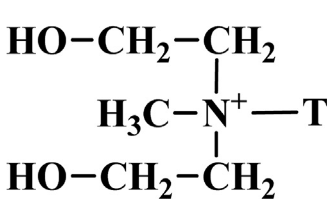

Fig. 1. Chemical structure of the montmorillonite modifier.T is Tallow (~65% C18; ~30% C16; ~5% C14).

2.3. Characterization methods

2.3.1. Rheological characterization

Viscosities of the freshly prepared epoxy–MMT systems were measured using a rotational rheometer Physica MCR-301 (Anton Paar, Austria). A cone-and-plate geometry was used (the cone diameter was 8 mm, the angle between the conical surface and the plate was 1°). Upward (at gradually increasing shear rate) and downward flow curves were obtained. Measurements were made at 20, 40 and 60 °C under constant shear rate conditions. The time interval between the sonication and rheological measurements was 1 h.

2.3.2. Lap shear strength characterization

Lap-shear adhesion strength was measured according to ASTM D1002-01 using an Instron-type testing machine. Crosshead speed was 10 mm/min. Steel tabs of 1.6 mm thickness were used for samples preparation. Samples were prepared with a 12.5 mm overlap. Before testing the tabs were roughened with sand paper and cleaned with acetone. Curing was carried out at 180 °C for 6 h at 0.1–0.3 MPa pressure.

2.3.3. TEM

Transmission electron microscopy (TEM) images were obtained with a LEO 912AB OMEGA (Germany–Switzerland) microscope. Ultrathin specimens were cut from adhesive films using a Reichert–Jung (Austria) microtome equipped with a diamond knife.

2.3.4. X-ray characterization

To evaluate the degree of exfoliation of clay and d-spacing between the clay platelets, XRD measurements were performed. An automatic difractometer DRON-2 ("Burevestnik", USSR) with CuKα radiation with modified collimation (to reduce the contribution of the stem radiation) was used. Modified collimation allows the device to recede the Bragg scattering contribution and to record reflexes starting from $2\Theta = 1°$.

Powders prepared from the cured systems were placed into a special metallic cell, measurements were made under reflection mode.

3. Results and discussion

3.1. Optimization of the clay dispersion conditions

3.1.1. Influence of pre-mixing time

Direct methods usually applied for composites structure investigation – XRD measurements, electron microscopy – are rather complex techniques. Moreover, they characterize the structure of the material at some local point, not the structure of the material in total. So, an indirect method was chosen to study the structure of the systems investigated – rheological measurements. Rheology of the suspensions is greatly affected by polymer–particle interactions and by the distribution of the particles in the system – as shown in the literature [20,24,25].

First of all, influence of the pre-mixing time on the viscosity vs. shear stress dependences was studied for the epoxy–MMT systems (Fig. 2).

It should be noted that the epoxy oligomer studied exhibits Newtonian behavior as has been shown by other researchers [12,13].

As expected, MMT incorporation into epoxy oligomer results in the viscosity increase of the system. Viscosity increases up to 3 times when 2 wt% of clay is added to the system. The increase