Epoxy reinforcement with silicate particles: Rheological and adhesive properties - Part II: Characterization of composites with halloysite

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ABSTRACT

Rheological and adhesive properties of epoxy oligomer–halloysite systems were studied. Ultrasound treatment of epoxy–clay systems was used for their homogenization. The results were compared with the data obtained earlier for epoxy resins filled with natural and organomodified montmorillonites (MMTs). Clear correlation between the rheological and bonded joint behavior of epoxy–halloysite systems was observed at 5 wt% of halloysite. A decrease in the viscosity of the systems and the yield stress values after sonication is shown to be caused by nanotube breakage and by formation of agglomerates when the broken nanotubes were lined up in the same direction. It leads to a remarkable drop in joint strength with increasing sonication time for 5 wt% halloysite systems. 2 wt% halloysite addition resulted in an ~30% increase in joint strength, which is less than in the case of MMTs incorporation.

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1. Introduction

Nanosized fillers for brittle polymers – especially epoxy resins – have been intensively studied in recent years in an attempt to improve the toughness of the matrix [1–16]. A lot of various fillers such as silica [7–9], montmorillonite, natural and organically modified [1–6], sepiolite [10], carbon nanotubes [13–17], etc. were studied. Significant toughness enhancement was obtained when MMT was used in an epoxy resin – for example, Basara et al. reports ~70% increase in the toughness of pristine epoxy resin when 0.5 wt% MMT was incorporated into the pristine matrix [1]. It should also be added that the MMT surface is often modified in order to obtain better interaction between hydrophobic polymers and hydrophilic clay. In some cases it leads to the MMT particles undergoing intercalation or exfoliation in the bulk of the polymer thus allowing further increase in toughness [1,4,6]. In the work carried out by Basara et al. [1] usage of organomodified MMT resulted in a ~130% increase in the toughness of unmodified epoxy resin at 0.5 wt% of filler content. However, there still exists the problem of the uniform MMT particles distribution, which is necessary to obtain enhanced properties.

Carbon nanotubes (CNTs) were also reported to increase the impact strength of epoxy resins at low modifier contents [13–17]. Similar to other filler types, nanotube distribution in an epoxy matrix remains an important issue and often functionalization of the nanotubes surface is used for this purpose [13,14,17].

Recently, halloysite nanotubes have become the subject of interest as a new promising filler for obtaining polymers with enhanced properties [11,12,18–23]. Halloysite nanotubes are easily obtainable – the same as MMT – and are much cheaper than carbon nanotubes. Moreover, halloysite nanotubes unique crystal structure is similar to the structure of CNT in terms of aspect ratio. They also possess high temperature resistant properties, hydroxyl group density on their surface is relatively low and certainly, presence of the nanoscale lumens should also be mentioned [18–26]. All these properties lead to various applications of the halloysite nanotubes for controlled drug and other active molecule release; halloysite nanotubes are also used as nanoreactors, adsorbents, nanofillers, etc. [24,25].

A number of researchers tested halloysite–epoxy systems and obtained toughened materials [11,12,19,21,22,27]. For example, Deng et al. [11] obtained up to a two-fold increase in the fracture toughness (G_{IC}) of an epoxy resin with 10 wt% of halloysite. Ye et al. [12] reported that the incorporation of halloysite (up to 2.3 wt%) led to an almost 400% growth in the Charpy impact strength. Toughening mechanisms were studied and identified as

combinations of micro-cracking/nanotubes bridging/pull-out/ breaking and crack deflection [11,12]. Recently, halloysite surface modification to enhance its dispersibility in polymer matrices was studied [18,20–22,27,28]. For example, usage of polyamidoamines grafted on the halloysite surface was reported in Ref. [27]. Unmodified halloysite incorporation resulted in an approximately 350% increase in the impact strength of an epoxy resin. Further increase (up to 2.5 times) in the impact strength of the system was obtained in the case of a polyamidoamine-grafted halloysite in comparison with the unmodified filler.

Certainly, not only the mechanical properties of systems with halloysite were improved. Increased thermal stability, flame and corrosion resistance of composites with halloysite were obtained [23]. Adding halloysite to epoxy resin was shown to increase dimensional stability of the system due to decreased coefficient of thermal expansion of the resin [19]. However, no data regarding the effect of halloysite incorporation on the adhesion properties of the epoxy resins have been found.

The main objective of our work was to study the influence of halloysite addition on the adhesion and joint strength characteristics of an epoxy resin and to compare the data obtained with those obtained for epoxy/MMT systems [29]. The influence of ultrasonic mixing on the structure and properties of the cured matrix was studied. Since the rheological properties of such systems are extremely sensitive to changes in the materials structure, their evolution with the addition of the filler and during sonication was considered as a marker of structural changes.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol-A epoxy resin based on DGEBA from EPITAL, Russia was used with the following characteristics: 185–190 g/eq weight for epoxide and epoxy groups content ~ 20 wt%. 4,4'-diaminodiphenylsulfone (DDS) from BASF, Germany was used as curing agent. The epoxy matrix was prepared using a ratio of 70/30 (w/w) epoxy resin/DDS.

The following nanofillers were used:

1) Halloysite, supplied by Sigma Aldrich, with 10 Å interlaminar spacing.
2) Carbon nanotubes, prepared at Mendeleev University of Chemical Technology of Russia, were used for comparison with halloysite tubes. The following characteristics of the nanotubes were provided by the producer: external diameter $10 \div 60$ nm, internal diameter $10 \div 20$ nm, length > 2 µm, apparent density 400–500 kg/m^3, specific surface area > 140 m^2/g.

Rheological measurements were made for epoxy oligomer-filler systems, containing 2 and 5 wt%, without curing agent. For carbon nanotubes only 2 wt% compositions were tested.

Systems with the curing agent were used to prepare samples for the lap-shear measurements.

2.2. Preparation of epoxy-filler compositions

Filler was mixed intensively with the epoxy oligomer at room temperature using an overhead stirrer for 15 min. Mixing time was chosen in accordance with the results of preliminary rheological testing described in [29]. Then the mixture was exposed to ultrasonic treatment by means of an ultrasonic disperser with an immersed waveguide for 2, 4 or 6 min. A waveguide with the following characteristics was used: 1.5 cm diameter, 22.4 kHz frequency, 100 W capacity. To prepare the samples for joint testing

the curing agent was added to the epoxy/filler system after the ultrasonic stirring and the composition obtained was mixed at room temperature with an overhead stirrer for five minutes. The compositions were then cured at 180 °C for 6 h.

2.3. Characterization methods

2.3.1. Rheological characterization

Viscosities of the epoxy–halloysite systems were measured using a rotational rheometer Physica MCR-301 (Anton Paar, Austria). A cone-and-plate geometry was used (the cone diameter was 50 mm, the angle between the conical surface and the plate was 1°). Upward (at gradually increasing intensity of shear) and downward (at decreasing intensity of shear) flow curves were obtained in the controlled rate and controlled stress modes. Measurements were made at 20, 40 and 60 °C.

2.3.2. Lap shear strength characterization

Lap-shear strength was measured according to ASTM D1002-01 using an Instron-type testing machine. The crosshead speed was 10 mm/min. Steel tabs made from 12X18H10T Russian grade steel (similar to A 109, Grade 2 steel recommended in the standard) with 1.6 mm thickness were used for sample preparation. Samples were prepared with a 12.5 mm overlap. The tabs used were roughened with sand paper and cleaned with acetone prior to formation of the bonded joint. Curing was carried out at 180 °C for 6 h at 0.1–0.3 MPa pressure. Tests were carried out at room temperature (22–25 °C) and humidity (~ 60%), with the joints being conditioned for 24 h at the given temperature and humidity prior to testing.

2.3.3. TEM

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

3. Results and discussion

3.1. Halloysite and carbon nanotubes characterization

TEM images of halloysite and carbon nanotubes, used in our experiments, are shown in Fig. 1. According to Fig. 1, similar tubular morphology of both fillers is clearly seen. Halloysite tubes inner diameter could be estimated as ~ 15–25 nm, external diameter as ~ 40–70 nm and their length as mostly 1000–2000 nm. Carbon nanotubes inner diameter could be estimated as ~ 15–20 nm, external diameter as ~ 30–100 nm and their length as mostly > 500 nm. It should also be mentioned that carbon nanotubes were more tangled than halloysite nanotubes (as expected) with a considerable number of small fragments being present which could be caused by the breakage of the long nanotubes into smaller fragments.

3.2. Rheological properties of epoxy oligomer–halloysite suspensions

As mentioned before, rheological measurements were used to characterize the structure of the epoxy/filler suspensions. Fig. 2 shows viscosity vs. shear rate dependencies of unsonicated epoxy–halloysite suspensions in comparison with similar dependencies for epoxy–MMT systems studied earlier [29].

As expected, clay incorporation into the epoxy oligomer results in a viscosity increase. However, whereas both types of MMTs cause similar, quite significant changes in the viscosity of pristine epoxy systems, halloysite influence on the viscosity of the epoxy