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The use of colemanite and ulexite as novel fillers in epoxy composites: Influences on thermal and physico-mechanical properties

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ABSTRACT

Boron compounds such as colemanite, tincal and ulexite are of interest in many application areas due to their great properties. Colemanite and ulexite was used individually as fillers to prepare epoxy composites in this study. The influences of amount of filler, type of hardener and plasticizer addition on the properties of the novel composites were investigated with instrumental analyses and tests. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses showed good dispersion of filler in the epoxy matrix. Improvement in tensile properties was obtained up to 5 wt% filler content in the composites. Water sorption reduced dramatically with increasing amount of filler compared to neat epoxy. Excellent corrosion resistance and strong adhesion properties were observed in all composites. Thermogravimetric analyses (TGA) and vicat softening temperature (VST) tests indicated that colemanite had better synergistic effect on the thermal properties of the neat epoxy than ulexite. Resistance to cold environment of the composites was quite high. It was thought that the composites can be evaluated successfully with the mentioned advantages in many industrial fields such as construction, coating, flooring, and so on.

1. Introduction

The application of polymer composites has significantly increased in many industrial areas such as aerospace, marine, construction [1], automotive, civil engineering structures [2], and sporting goods [3]. The polymer composites are widely used with their advantages of high mechanical strength, good damping properties [4], corrosion resistance [5] and design flexibility instead of conventional materials [6]. Polymer composites compose of filler and polymer matrix like thermoplastic, thermoset and elastomer [7]. Epoxy resins (ERs) are one of the most important thermoset matrices due to their remarkable properties including good mechanical and electrical strength [8], excellent adhesion capacity, high thermal and chemical resistance, low shrinkage [9] and processability [10]. In spite of these advantages, ERs have some adverse properties such as low thermal conductivity [11], high flammability [12] and brittleness [13] that restrict their applications. Fortunately, different types of filler are commonly utilized to overcome these drawbacks of the ERs [14]. Excellent matrix-filler compatibility can provide to improve toughness, mechanical properties [15], heat dissipation, electrical insulation [16] and flame resistance of the composite materials [17].

The most critical boron mineral reserves are located in the United States of America [18] and Turkey, especially around Bigadiç-Balıkesir, Emet-Kütahya and Kestelek-Bursa in the world [19]. The valuable boron compounds are colemanite ($Ca_2B_6O_{11}\cdot 5H_2O$), tincal ($Na_2B_4O_7\cdot 5H_2O$) and ulexite ($NaCaB_5O_9\cdot 8H_2O$) that have found various areas of usage [20]. Consumption of these boron compounds generally occurs in agriculture, textile, cleaning and bleaching products [21] in addition to glass, ceramic and nuclear industry. Moreover, they can be extensively favored as flame retardant in many material production and fuel for rocket motors [22]. There are considerable studies regarding the evaluation of boron compounds in the literature. Gencel et al. [23] investigated the effect of hematite and colemanite on the mechanical properties of polymer concretes containing silica sand as aggregate and ER. Celik et al. [24] prepared the new lightweight brick added colemanite and compared the physico-mechanical properties (compressive strength, ultrasonic transit speed, porosity, heat and sound conductivity etc.) of new brick with commercial lightweight bricks. Korkut et al. [25] studied neutron shielding properties of

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colemanite, ulexite and tincal based on number of boron atoms by using experiment and simulation process. Binici et al. [26] used colemanite, barite, ground basaltic pumice and ground blast furnace slag as additives in the production of mortars and determined mechanical and radioactivity shielding performances of the mortars. Cosansu et al. [27] evaluated colemanite powder as an abrasive in abrasive waterjet cutting (AWJC) with different traverse rate and abrasive flow rate and compared its performance with garnet which is well-known abrasive in AWJC process. Kaynak et al. [28] utilized colemanite as flame retardant in high-impact polystyrene containing brominated epoxy and antimony oxide. Isitman et al. [29] purposed to enhance flame retardancy of low-density polyethylene with adding combination of aluminum hydroxide and colemanite. Baştürk et al. [30] tried to improve mechanical, thermal and surface properties of bisphenol A dicyanate ester with bisphenol P dicyanate ester and colemanite. In the grand scheme of these studies mentioned above, boron compounds are especially effective to improve thermal stability and prevent radiation transmission with important lightweight and cost benefits. However, certain percentages of boron compounds can cause a decrease in mechanical strength of the materials.

In spite of many published studies related with epoxy composites, any work has not been reported with details based on epoxy composites including colemanite and ulexite fillers. From this point of view, epoxy composites were prepared with two novel fillers at different compositions. In this study, it was aimed that investigation of effects of some parameters such as amount of filler, type of hardener and addition of plasticizer on the properties of the composite materials. And so, the morphological, physico-mechanical and thermal properties of the composite materials were determined and compared with neat epoxy and each other.

2. Experimental

2.1. Materials

Bisphenol A epoxy resin with an epoxy equivalent weight of 184–190 g/equiv was used as matrix system. Colemanite and ulexite as filler was supplied from Eti Mine Boron Works, Turkey. These boron compounds had particle size <140 mesh and the chemical composition of colemanite and ulexite were B_2O_3 49.17%, CaO 26.71%, Na_2O 0.25%, MgO 1.27%, SiO_2 2.95%, LOI 19.01%, and B_2O_3 42.98%, CaO 13.80%, Na_2O 3.20%, MgO 0.46%, SiO_2 1.78%, LOI 35.90%, respectively. Two types of hardener which was commercially known as Epamine PC 17 based on aliphatic amine structure and methylnadic anhydride (MNA) were used. Polyethylene glycol (PEG) with average molecular weight of 380–420 g/mol and 2,4,6-tris(dimethylaminomethyl)phenol were utilized as plasticizer and accelerator, respectively.

2.2. Preparation of the epoxy composite materials

Colemanite/ER composites (CECs) and ulexite/ER composites (UECs) were prepared in the same experimental procedure. Filler (0, 3, 5, 10 and 20 wt%) and ER were mixed with mechanical stirrer after avoiding moisture content of the filler. Sonication was carried out to remove entrapped bubbles in the each blend in addition to providing chain mobility to ER and 25 wt% of Epamine PC17 was added to the blends. The accelerator was dropped to all blends and the blends were immediately poured into the mold prepared according to ASTM D 638 Standard [31]. The curing and post-curing process were set as for 4 h at 40 °C and for 4 h at 80 °C in an oven. Following the same procedure, composite materials were obtained with 30 wt% of MNA. The mold was kept for 12 h at 60 °C followed by post-curing for 12 h at 120 °C. The other composite material series were prepared with the addition of PEG by fixed 5 wt% into the blends. Three replicate samples of each composite material were prepared to get reliable results.

2.3. Characterization of the epoxy composite materials

XRD patterns were investigated by Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54060$ Å) over a 2θ range of 20°–80°. The surface morphology was characterized by SM Zeiss LS-10 scanning electron microscope at an accelerating voltage of 20 kV. Before SEM analysis, the samples were sputtered with gold to provide surface conductivity. The tensile tests were carried out by using Stretch and Pressing Equipment TST-Mares/TS-mxe at a cross-head speed of 5 mm/min. Hardness test was performed using Shore Durometer TH 210. Water sorption was investigated with immersing each sample in water for two weeks at room temperature according to ASTM D 570 Standard [32]. The samples were taken out periodically and dried with a dry cloth, and then immediately weighed. The percentage of water sorption was calculated using the following equation:

$$Water\ sorption\ (\%) = \left[\frac{W_t - W_0}{W_0}\right] \times 100 \tag{1}$$

where W_t is the weight of the sample at time t and W_0 is the initial weight of the sample. Corrosion test was carried out with immersing each sample in 3% NaCl, 10% H_2SO_4, 10% NaOH and water for two weeks at room temperature [33]. The performance of each composite material against corrosion was evaluated visually. Adhesion test was applied to each sample according to Lattice notch method [34]. The pre-prepared blends were coated as a thin layer on the clean stainless steel metal surfaces and these layers were exposed to same curing process conditions with composite material preparation. The layers were divided into squares (1 mm × 1 mm) with razor blade, and then a sticky tape was applied over the squares. The sticky tape was suddenly pulled out. While many squares were still on the metal surface, some of them separated from the surface. The percentage of adhesion was calculated using the following equation:

$$Adhesion\ (\%) = \left[\frac{a - b}{a}\right] \times 100 \tag{2}$$

where a is the total number of squares on the metal surface and b is the number of squares separated from metal surface. TGA analyses were performed on Lab. METTLER STAR SW thermal analyzer at a heating rate of 10 °C/min from 25 °C to 600 °C under a nitrogen flow. VST and density was determined by CEAST HDT Vicat analyzer with 50 N loading at a constant heating rate of 50 °C/h according to ASTM D 1525 Standard [35]. Cold resistance test was conducted with keeping each sample for 24 h at −25 °C in a fridge according to TSE K 86 Standard [36]. Physical appearance of each composite material was observed visually.

All characterization tests mentioned above were carried out three times on each sample and the arithmetic average values were calculated and presented.

3. Results and discussion

Fig. 1 shows XRD patterns of neat epoxy, colemanite and CECs hardened with two different hardener. It can be seen that the colemanite had sharp diffraction peaks between 20° and 50°. Many diffraction peaks of the colemanite were disappeared and the others became to quite smaller peaks with the incorporation of colemanite to ER hardened with Epamine PC 17. It indicated