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Organic montmorillonite reinforced epoxy mortar binders

Yifan Sun [a], Ke Xu [a], Yuge Zhang [a], Jing Zhang [a], Ru Chen [a], Zuanru Yuan [b], Hongfeng Xie [a,*], Rongshi Cheng [a,c]

[a] MOE Key Laboratory of High Performance Polymer Materials and Technology, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China
[b] Modern Analysis Center, Nanjing University, Nanjing 210093, China
[c] College of Material Science and Engineering, South China University of Technology, Guangzhou 510641, China

HIGHLIGHTS

- OMMT/EMBs for pavements on orthotropic steel bridge decks have been developed.
- Epoxy chains have been intercalated into the OMMT layers.
- Homogenous dispersion of OMMT in EMB matrix has been observed.
- The addition of OMMT improves the thermal and mechanical properties of the neat EMB.

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ABSTRACT

In this work, in order to investigate the reinforcement effects of organic montmorillonite (OMMT) modified epoxy mortar binders (EMBs), a series of OMMT/EMB composites with different OMMT loadings were prepared. The structure and thermal stability of OMMT were studied by X-ray diffraction (XRD), Fourier transform infrared spectrum, and thermogravimetric analysis (TGA). The effects of OMMT on the structure, glass transition, damping properties, thermal stability, mechanical properties and morphology of EMB were characterized by XRD, dynamic mechanical analysis, TGA, tensile test, and scanning electron microscopy. XRD results indicated that epoxy chains intercalated into the OMMT layers and led to the expansion of OMMT layer spacing. The presence of OMMT increased the glass transformation temperature, crosslink density of the neat EMB. Furthermore, the incorporation of OMMT improved the thermal stability of the EMB. The OMMT/EMB composites showed higher tensile strength and Young's modulus than the neat EMB. Homogenous dispersion of OMMT in EMB matrix was observed.

1. Introduction

Polymer mortars are concrete-like composites which are made up of polymer binders and aggregates. They have been widely applied in construction industry and building materials all over the world [1–4]. Epoxy resin is one of the most used polymer binder because of its irreplaceable advantages, such as excellent strength and durability, low cure shrinkage, perfect compatibility and so on [5]. These properties supply high value-added applications in many industries engaged in product assembly, including aerospace, civil engineering, automotive, chemical, electrical, marine, leisure, and many others.

Nanoclays are made extensive use of to promote the thermal and mechanical properties of the polymer matrices [6–8]. Montmorillonite (MMT) is a kind of nanoclay with a 2:1 layered structure, which has been conventionally used in the modification for the polymers [9]. Since MMT first introduced the Nylon-6 at Toyota Central R&D Labs in 1985, great interests have been generated to use MMT as nanofillers to prepare polymer composites [10]. Recently, much attention has been paid to preparation and characterization of epoxy/MMT composites. For example, Kaynak et al. [11] reported the epoxy resin/MMT composites with remarkable enhancement in flexural strength and stiffness by in-situ intercalative polymerization. Gârea's group found the MMT could be better intercalated by the epoxy resin pretreated with polyetheramine than the raw epoxy resin [12]. In order to increase the compatibility between the inorganic phase and polymer matrix phase, MMT layer structure has been often organically modified. The effect of mixing sequences for the epoxy/organic montmorillonite (OMMT) system was studied by Yap and Chow [13]. Their experiments demonstrated the dispersion and intercalation of OMMT could be effected by the mixing sequence. The addition of OMMTs enhanced the thermal stability of epoxy resin [14].

* Corresponding author.
E-mail address: hfxie@nju.edu.cn (H. Xie).

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Recently, epoxy mortar binder (EMB) has been widely used on the pavement of the long-span steel bridge [15]. However, until now, there are few studies on the effects of OMMT on the properties of EMB as far as we know. In the present work, OMMTs were incorporated into EMB as nanofillers. The glass transition temperature (T_g), damping properties, thermal stability, tensile properties of OMMT/EMB composites were characterized.

2. Materials and methods

2.1. Materials

The two-component EMB was prepared in our laboratory. The properties of the two components, that is, epoxy resin and curing agent are listed in Table 1. The mass ratio between epoxy resin and curing agent is 49:51. Organic montmorillonites (OMMTs, DK4) were supplied by Zhejiang Fenghong New Material Co., Ltd. (China). The OMMT is Na^+-montmorillonite ion-changed with dioctadecyl dimethyl ammonium bromide, which cation exchange capacity (CEC) is 100–120 meq/100 g. The properties of OMMTs are demonstrated in Table 2.

2.2. Preparation of the OMMT modified epoxy mortar binders

The cure agent and OMMTs were mixed in a 100 ml round-bottom flask with magnetic stirring at 120 °C for 3 h. Then mechanical agitation was adopted to blend the epoxy resin and above prepared mixture in a 200 ml beaker for 3 min at a stirring rate of 2000 rpm. After the above procedure, polytetrafluoroethylene (PTFE) molds were used to contain the mixtures for curing procedure in the oven at 60 °C for 3 days. The OMMT loading in EMB composites was 0, 2, 4 and 8 weight percent (wt%) of OMMT/EMB composites, respectively.

2.3. Tests and measurements

Fourier transform infrared spectrum (FTIR) was tested by NEXUS 870. The OMMT powder sample was first prepared as KBr pellet before test. The examination range was from 400 to 4000 cm^{-1}.

X-ray diffraction (XRD) test was implemented with the crystal monochromated CuKα radiation. The test device was Shimadzu XRD-6000 and the test range was between $3° < 2\theta < 40°$. The scanning rate was 5°/min.

The dynamic mechanical analysis (DMA; DMA + 450, 01 dB-Metravib, France) was conducted to evaluate the T_gs of the OMMT/EMB composites. The test mode was tension mode. The specific parameters were the heating rate of 2 °C/min, the test temperature range from −40 °C to 50 °C and the frequency of 1 Hz.

Thermogravimetric analysis (TGA, PerkinElmer Pyris 1 TGA) was measured from 25 °C to 700 °C at a 20 °C/min heating rate. During the heating process, the test was under a nitrogen atmosphere.

Tensile test was carried out on Instron 4466 universal testing machine. Referring to ASTM D638, the strain rate was 500 mm/min and the strain force was 500 N. The samples were cut by the dumbbell cutter into 5 mm × 56 mm. Through the whole test, the test temperature was kept at 23 °C.

The scanning electron microscopy (SEM, Hitachi S-4800) was adopted to observe the morphology of OMMT and the OMMT/EMBs. Before observation, gold was coated on the OMMT powders and liquid nitrogen fractured OMMT/EMB composites.

3. Results and discussion

3.1. Characteristics of OMMTs

3.1.1. FTIR

The FTIR spectrum of the OMMT is demonstrated in Fig. 1. As MMT absorbs the water easily, the broad band at 3400 cm^{-1} is ascribed to the water hydrogen bonded. Furthermore, four characteristic peaks presented in the spectrum indicate the stretching of –OH (3626 cm^{-1}), the bending of H–O–H (1649 cm^{-1}), the stretching of Si–O (1034 cm^{-1}), the stretching of Al–O (523 cm^{-1}) and the bending of Si–O (461 cm^{-1}). Above peaks also can be found in the raw MMT [16], and OMMT owns the other three unique peaks which exhibit the superficial organic matter: the C–H asymmetric and symmetric stretching (2926 cm^{-1} and 2850 cm^{-1}) and the –CH_2– scissoring vibration (1477 cm^{-1}).

Table 1
Properties of epoxy resin and curing agent.

Property	Value		Test method
	A	*B*	
Viscosity (23 °C, mPa · s)	4210	44	ASTM D445
Specific gravity (23 °C, g/cm^3)	1.15	0.97	ASTM D1475
Equivalent weight (g/eq)	204	234	ASTM D1652

3.1.2. Thermal stability

The TGA and derivative thermogravimetric (DTG) curves of OMMT are plotted in Fig. 2. It can be seen that the thermal decomposition of OMMT includes three steps: loss of free water (lower than 200 °C), loss of organics and interlayer water (250–400 °C), and loss of bound water (400–550 °C) [17]. Furthermore, the char residue at 600 °C for OMMT is 53.9 wt%, which much lower than that of the pristine MMT (68.7%) reported by other researchers [18].

3.1.3. Morphology

SEM was used to observe the microstructure of OMMT. The SEM microphotography of OMMT is showed in Fig. 3. It can be observed that silicate nano-layers of OMMT are exfoliated into individual lamellae. It is believed that the exfoliated state of MMT is helpful to maximize interfacial contact and interaction between polymer matrix and layered-silicates and result in homogeneous dispersion of OMMT in the polymer [19].

3.2. Characterization of OMMT/EMB composites

3.2.1. X-ray diffraction

The variation of the distance between silicate layers in the polymer was observed by XRD. Fig. 4 illustrates the XRD patterns of OMMT and OMMT/EMB composites. The d_{001}-reflection peak of OMMT appears at 4.84° (2θ). Based on the Bragg equation, the calculated interlayer spacing of OMMT is 1.82 nm, which is much higher than that of pristine Na-MMT (1.14 nm) [20]. This indicates that the interlayer spacing of clay layers increases nearly 60% with organic modification of the pristine MMT. For the OMMT/EMB composites, the d_{001}-reflection peaks appear at 3.86–3.90°, corresponding layer spacings are from 2.28 to 2.26 nm. Obviously, epoxy chains intercalate into the gap of the OMMT layers and result in more than 25% expansion of layer spacing [21]. Furthermore, like OMMT, the curves of OMMT/EMB composites can be observed three obvious peaks, which indicate that the layered structure of OMMT has not been destroyed by the intercalation of epoxy chains. For EMB composites, the d_{001}-reflection peak slightly transfers to higher degree with the increase of OMMT loading due to negligible agglomeration of OMMT in the epoxy matrix [22].

3.2.2. Dynamic mechanical properties

The storage modulus (E'), T_g, and damping properties of the neat EMB and OMMT/EMB composites were studied by DMA. The curves of storage modulus and tan δ versus temperature for the OMMT/EMB composites are demonstrated in Fig. 5. The E' relates to the energy stored in the polymer material [23,24]. Tan δ relates to the glass transition and damping properties of materials. The peak temperature in a tan δ versus temperature curve is defined as the T_g of a material. The results of E' and T_g are summarized in Table 3. It can be seen from Fig. 5b that the peak of tan δ slightly shifts to higher temperature with the increase of OMMT loading, which indicates that the presence of OMMT enhances the T_g of the neat EMB (22.85 °C) and the T_gs of OMMT/EMB composites increase with OMMT loading.

It is well known that the T_g of epoxy resin relates to the crosslinking density of epoxy network [25,26]. The crosslink density (v_c) of the neat EMB and OMMT composites listed in Table 3 were calculated by Eq. (1):