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Article

Facile Synthesis and Synergistic Effect of Calcium Sulfate Fillers on the Adhesive Properties of Bisphenol A (DGEBA) Epoxy Resin

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Abstract: The synergist effect of calcium sulfate fillers on epoxy resin's adhesive properties with calcium sulfate fillers was evaluated. It is learned that the porosity of modified calcium sulfate fillers resulted in the achievement of a high tensile modulus. The addition of calcium sulfate fillers significantly increased the tensile modulus at lower wt % and achieved high crystalline $CaSO_4$ composite. The scanning electron microscopy (SEM) shows an even distribution of concentrated $CaSO_4$. Clusters formed at higher $CaSO_4$ ratios produced large expansion, low crystallinity, and increased elongation. Further, it was observed that even distribution and dispersion of fillers enhanced transformation, greatly improved and enriched epoxy resin's bonding performance in the interfacial area. Enhancing the mechanical properties of epoxy resin via $CaSO_4$ fillers have broadened applications prospect in environmental fields. This suggests and encourages the widespread use of $CaSO_4$ fillers in environmental engineering in terms of adhesive properties.

Keywords: Calcium sulfate fillers; tensile modulus; scanning electron microscopy; elongation.

1. Introduction

Calcium sulfate ($CaSO_4$) was introduced as a backbone substitute materials in 1892 by Dreesman, and Peltier introduced as a sustainable material for filling bone defects in 1961 [1]. It also used as painting [2,3], and indoor building decorative material and efforts are continued to reduce the

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outdoor costs [4,5]. Recently, calcium sulfate fillers have been used to enhance thermoplastic stress and strain, such as; heat distortion temperature, hardness, stiffness, shrinkages [6-8]. Industry and academia are too busy carrying out experiments with the common practice of adding different fillers materials to improve the adhesive properties of the thermoplastics such as stress and strength [9,10]. Calcium sulfate semi-hydrated and calcium sulfate dehydrated are widely used in construction and building materials [11,12]. $CaSO_4$ fillers have good thermal stability, satisfactory bio-compatibility with strong potential applications [13,14]. It has a very high decomposition temperature, making it significant for developing new ways for its efficient utilization [15,16] hair shaped like $CaSO_4$ fillers with many ideal characteristics such as; high strength and high stiffness make them excellent fillers for matrix [17,18]. It can be easily derived from renewable agriculture, which consumes CO_2 and saves a significant amount of energy [19,20]. Fillers surfaces modification improved its dispersion in the polymer matrices and the interfacial interactions [21,22]. Calcium sulfate; a by-product formed in the process of purification of lactic acid monomer and can be used for the modification of polylactic acid (PLA). In addition, this filler improved the PLA's impact resistance and water vapor delivery performance in the packaging industry [23,24]. Calcium sulfate is a common inorganic compound with great environmental and industrial importance and exists a massive scale in nature [25-27]. Further studies on the sealing aspect of calcium sulfate $CaSO_4$ fillers have opened new ways to detect and assess metal surfaces' large scale formation [28]. Synthesis of gypsum-based materials further widened the application value of gypsum ($CaSO_4$ fillers), extremely safe, highly biocompatible, bio-resorbable, and osteoconductive, and potentially act as a good carrier [29-31]. The performance is closely related to its watering product setup speed, good operability, high strength, its micro-size, and is widely used in the construction industry [32,33]. In the medicinal field, calcium sulfate fillers are also improving antibacterial treatment efficiency, especially in orthopedic surgery and biomimetic materials and especially tissue engineering scaffolds [34,35]. It is well known that the surface free energy of needle-like $CaSO_4$ fillers is very high, instability in polymers, and making them incompatible. With poor dispersion, it makes composites low-performance unattractive materials [36-38].

The purpose of this article is to investigate the surface property and mechanism of native $CaSO_4$ fillers, modified $CaSO_4$ fillers, and KH-560 coupling agent promoting the interfacial bonding and compare the mechanical properties. TGA and SEM were used to understand the surface properties of composite material. The FTIR studies of $CaSO_4$ fillers confirmed the presence of various functional groups in modified $CaSO_4$ fillers. This modification approach provides a novel and meaningful way for the modifier selection of $CaSO_4$ fillers. The surface morphologies of homogeneous mixtures were observed by SEM. This study aims to present some new at environmentally friendly strategic pathways to modify, prepare, and characterize $CaSO_4$ fillers and found effective for adhesives properties and thermal conductivity. In this approach, $CaSO_4$ fillers coated on steel plates, enhanced the interfacial adhesion property, and assumed to be favorable for composites preparation with boosted thermal properties. The influence of modified $CaSO_4$ fillers on the dispersion properties comprehensively investigated and found exhibiting better properties, such as better tensile modulus, tensile strength, and elongation.

2. Materials and Methods

2.1. Materials.

Native calcium sulfate N-$CaSO_4$ fillers, with the diameter of the particles about 1-4 μm having a loose density from 0.1-0.4 g/cm^{3,} was supplied by Zhengzhou bokaili ecological engineering, liyang Zhengzhou city, Henan province China. Analytical pure reagents, including ethanol, acetone, and acetic acid, were obtained from the Aladdin reagents Shanghai industry. Chemicals were used without further purification. $CaSO_4$ dried at 80 °C for 8 h in the vacuumed oven to remove the moisture prior to its use. Then stored the remaining product in a desiccator prior to use

2.2. Modification of calcium sulfate $CaSO_4$ fillers with silane.

Firstly, 100 mL of distilled water and 5 mL of 3-ethyl propyl silane were added into a 150 mL three-necked flask and stirred for 1 hour at 80 °C to conduct hydrosilylation of KH-560. Added 0.3 g of $CaSO_4$ fillers to the mixture, and placed at supersonic speeds for 20-30 minutes to get well disperse. Then the mixture stirred at room temperature for the next 150 minutes. Centrifuged and cleaned with ethanol (2 times) and water to remove excess silane. The resulting product dried for 4-5 hours in a hot air furnace at 80 ˚C. The product stored in a glass bottle for further use and labeled as M-$CaSO_4$.

2.3 Epoxy resin.

Recent progress has been made in epoxy resins, particularly the bisphenol A epoxy resin (DGEBA) in Figure 1. Epoxy resins are widely used in commercial paintings, adhesives, military carbon-fiber-reinforced high-performance composite materials, and other fields to improve materials' properties [39]. Most epoxy resins are made from petrochemicals with limited resources, such as bisphenol BPA, bisphenol BPS, bisphenol BPF and novolacs. DGEBA can use different curing agents, such as amines, imidazoles, anhydrides, etc. Among them, bisphenol A diglycidyl ether can be easily cured [40-42].

2.4 Treatment of Calcium sulfate $CaSO_4$ fillers with epoxy resin and preparation of steel plates.

The Calcium sulfate ($CaSO_4$) fillers dispersed in the epoxy resin, used triethylenetetramine (TETA) as curing agent and evaluated for their adhesives and thermal conductive behaviors. The steel plate was polished with sandpaper, dry at room temperature, and stored in a plastic bag for further use. The steel plate polished and tested 3 times before the test according to the method for $CaSO_4$ fillers adhesive performance determination. Epoxy resin 1 g and $CaSO_4$ fillers with 1,3 and 5 wt % respectively, were put in the sample glass bottle, and then stirred at room temperature for the next 3 hours. After that, 0.2 g of TETA was slowly injected and stirred for the next 10-15 min until it got a completely homogenous mixture. The mixture vacuumed for 15-20 min in the oven at 45 ˚C to remove the bubbles from the solution and poured the entire mixture on steel plates 1.5 cm long and 2.3 cm wide. Cure in the oven for 1 hour at 120 ˚C. After that, the steel plates sample cold down at room temperature. Standard test boards were placed at room temperature for 2-3 days prior to testing.

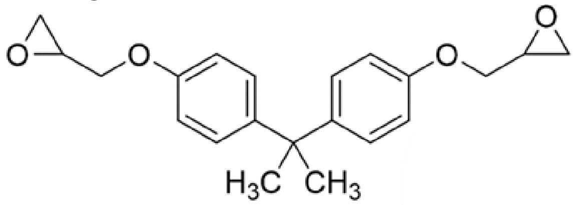

Figure 1. Bisphenol A diglycidyl ether.

2.5. Characterization.

Samples characterization carried through different spectroscopic techniques, including Scanning Electron Spectroscopy (SEM), Thermal Gravimetric Analysis (TGA), and Fourier Transform Infrared (FT-IR) spectroscopy. Tensile modulus and strength (model Z020, Zwick/Roell) used to analyze $CaSO_4$ fillers dispersion and adhesion in the epoxy resin.

3. Results and Discussion

3.1 Chemical modification of calcium sulfate $CaSO_4$.

The broad peak appeared at 2860 cm^{-1} was assigned to C-H stretching vibration. The peak appeared at 1470 cm^{-1} attributed to C-H bending vibration. The peak appeared at 1370 cm^{-1} was ascribed to C-H bending vibration peaks confirmed the successful modification of calcium sulfate $CaSO_4$, as shown in Figure 2. [43,44].

3.2. Thermal properties of calcium sulfate.

The thermos gravimetric analysis of calcium sulfate (Native and Modified), as shown in **Figure 3** is a dynamic phonological method to understand the reaction of temperature changes [45,46]. Thermal degradation occurs between 300 ˚C and 600 ˚C temperature ranges because of its high thermal stability to nanoscale size. $CaSO_4$ chain shows a significant reduction in molecular weight degradation in high sulfate amorphous regions. The $CaSO_4$ showed that decomposition started at 240 ˚C to 360 ˚C and left a small amount of ash at 550 ˚C. The activation energy of calcium sulfate mortification is significantly reduced by the introduction by hydrolyzed sulfate groups [47]. In addition, the decomposition of calcium sulfate at 320 ˚C also indicates fast heat transfer. Calcium sulfate fillers formed clusters and resulted in higher thermal conductivity [48]. The lower weight loss of native $CaSO_4$ indicates that nearly one-third of the mass is still in the residue.

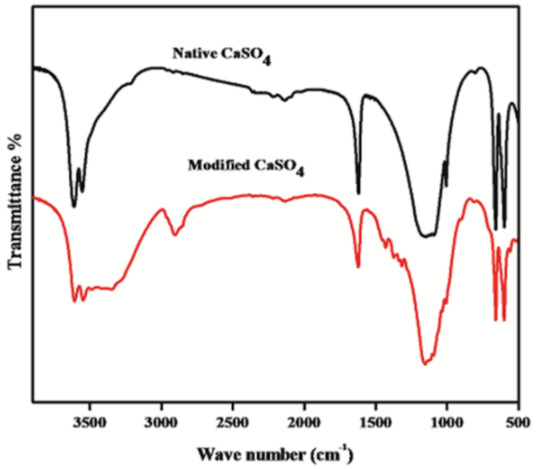

Figure 2. FTIR, N-$CaSO_4$, and modified M-$CaSO_4$.

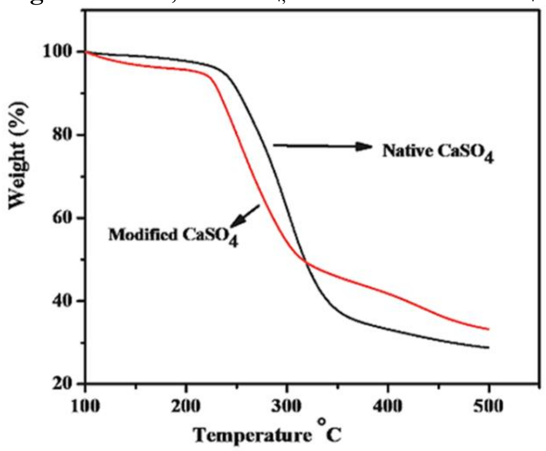

Figure 3. TGA of N-$CaSO_4$ and modified M-$CaSO_4$.

3.3 X-ray powder diffraction XRD.

Native and modified calcium sulfate fillers were studied by X-ray powder diffraction XRD as shown in Figure 4. Microstructure parameters, including crystallite size and micro stress values, were determined by using the Williamson-Hall Plot. It has been established that Native and modified calcium sulfate fillers are characterized by a similar size of crystals, and the main contribution to the broadening of diffraction peaks is attributable to micro stress in the studied materials. XRD spectra of a precipitate isolated from solution after approximately 1 minute showing the presence of both hemihydrate peaks. A mixture was obtained due to the time taken to filter the volumes of the solution required to give sufficient analysis material. The structure was further examined by powder XRD. Diffraction patterns were compared with the reference standard. All of the detected diffraction peaks are indexed to modified calcium sulfate fillers, which is in good agreement. It can be seen that several weak broadening diffraction peaks of the sample modified by coexisting with the characteristic peaks of Native calcium sulfate fillers [49,50].

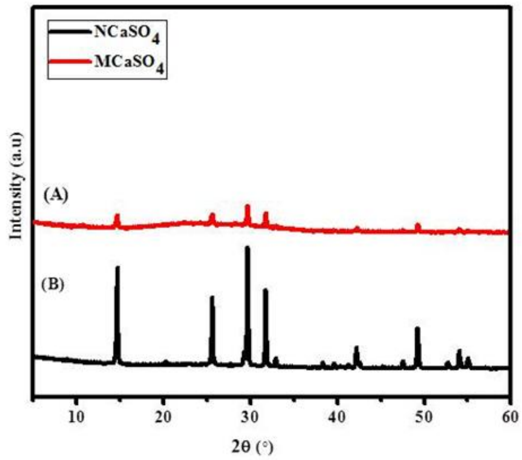

Figure 4. XRD analysis of N-$CaSO_4$ and modified M-$CaSO_4$.

3.4 Scanning Electron Microscope.

The SEM images were obtained on a field emission scanning electron microscope (FE-SEM, SU-3500), after sputter coating of gold on the specimen's surface. The morphologies of the surface images of $CaSO_4$ were exhibited reasonable adhesion properties, homogeneous dispersion in the mixture, and observed surface morphologies of different samples with the difference calculated amount of $CaSO_4$ dispersed in epoxy resin [51-53]. The surface of native calcium sulfate fillers (N-$CaSO_4$) looks very clear (Figure. 5a), and after modification (M-$CaSO_4$) looks clear without epoxy, but their diameter decreases after modification with (KH-560) coupling agent to various degrees (Figure. 5b).

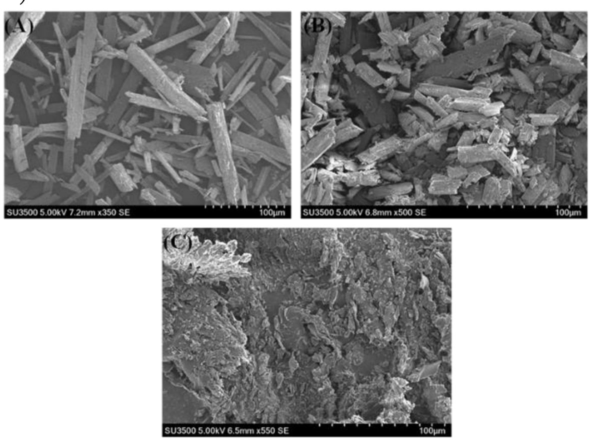

Figure 5. FE-SEM, SU-3500, (A) N-$CaSO_4$ (b) M-$CaSO_4$ (C) Modified materials treated with epoxy resin.

However, with additional calcium sulfate fillers, the agglomeration occurs to prevent the formation of homogeneous mixtures (Figure. 5c). Modified materials treated with epoxy resin significant improved interfacial adhesion reflect the rough surface layer, increasing the tensile modulus and tensile strength. In general, their combination has an increase in the adhesive properties and has a favorable effect on the composites [54,55,22]. The porosity of the modified mixture of M-$CaSO_4$ was determined to be 2330 (Tensile modulus MPa) and 14.70 (Tensile strength MPa), respectively, which indicates an insignificant difference in the total porosity of the mixtures [56,57].

3.5 Adhesive Properties

It is very important to study the bonding properties (native and modified) of calcium sulfate fillers. The average mechanical parameters are summarized; tensile modulus, tensile strength, and elongation fracture are enhanced compared with epoxy resins with respect to the content of $CaSO_4$ with different wt % ratios (Figure. 6). Epoxy resins containing $CaSO_4$ (native and modified) were evaluated at concentrations of 1 wt, 3 wt, and 5 wt % to comprehend the modification's impact on its enhanced perspective.

Tensile modulus (MPa) of $CaSO_4$ (Native & Modified), under heavy load of stretched steel plates and sample specimens, the modified $CaSO_4$ had a significant enhancement in all wt % concentration, especially on 1 wt % modified $CaSO_4$ show high tensile modulus ratio in comparison with the other modified $CaSO_4$ (Figure. 6A). Optimal modified $CaSO_4$ (1 wt %) content distribution of fillers in the epoxy matrix causes tensile modulus property [58,59].

In comparing native $CaSO_4$, the tensile strength of M-$CaSO_4$ load transfer and enhancement performance is due to the possibility of fillers dispersion and modified particles in the epoxy matrix (Figure. 6B), resulting in high-stress transfer [60,61]. Interestingly, the pull and tensile strength of native $CaSO_4$ increased by 5 wt% compared to the modified $CaSO_4$. The strength is greatly enhanced by native $CaSO_4$ and epoxy. However, these two levels showed a similar swelling effect. It is worth mentioning that it is highly hydrophobic and is more compatible with the epoxy matrix [62,63].

Overall, the mechanical performance tests have given good compatibility from epoxy to $CaSO_4$ (native and modified). The highly modified M-$CaSO_4$ has a significant lysing rigid structure that enhances the filler's rigidity because it increased both the tensile modulus and strength contrast to the native tensile modulus and tensile strength of calcium sulfate fillers. Since calcium sulfate fillers are generally breakable medium, this additive can be used in some practical applications.

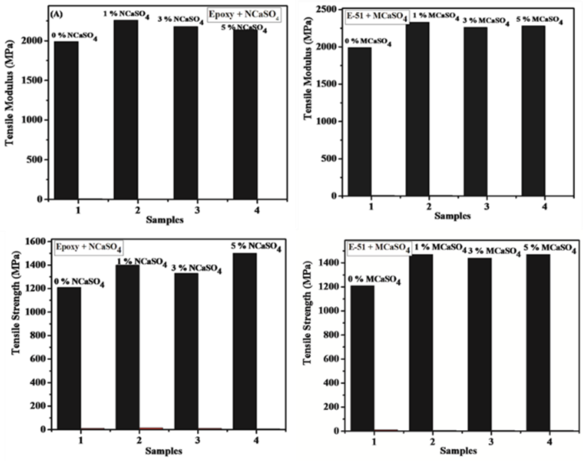

Figure 6. Adhesive strength of Native and Modified $CaSO_4$.

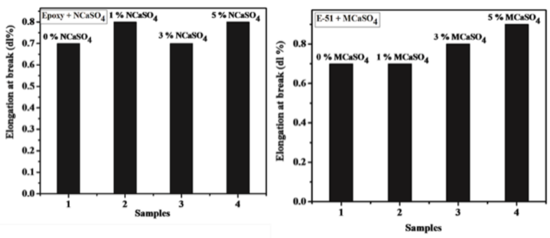

Figure 7. Representation of elongation at breaks of (C) N-$CaSO_4$ & (D) M-$CaSO_4$.

3.6. Elongation at the break.

Elongation fracture compared to a standard sample. The rate of calcium sulfate $CaSO_4$ (native and modified) composite is increasing, and reaches a maximum of modified $CaSO_4$ 5 %, compared with native $CaSO_4$. Comparing the increase of 5 % M-$CaSO_4$ load elongation with the native $CaSO_4$ plays an important role in stress concentration. Due to a strong interface between calcium sulfate and epoxy resin's adhesion, the stress between them can be effectively transmitted [22,23]. Therefore, it is not possible to have to debond between $CaSO_4$ and epoxy resin. Stress concentration will affect the abrupt of calcium sulfate at break elongation under high load. On the other hand, calcium sulfate can significantly enhance the epoxy chain, which greatly enhances the interfacial adhesion. Figure 7.

Representation of elongation at breaks of (C) N-$CaSO_4$ & (D) M-$CaSO_4$.

4. Conclusions

Adhesive properties of epoxy with $CaSO_4$ (native & modified) are presented in this article. The modified $CaSO_4$ has better porosity than native $CaSO_4$. The most promising finding is the achievement of a high tensile modulus. The addition of $CaSO_4$ composites could significantly increase the tensile modulus at lower wt % and achieved the maximum crystallinity of modified $CaSO_4$. Considering the advantages of $CaSO_4$, the scanning electron microscopy showed even the distribution of $CaSO_4$ fillers. However, clustering was observed at higher $CaSO_4$ ratios. The composite content matrix with high $CaSO_4$, produced good expansion, low crystallinity, and increased tensile modulus and tensile strength. It is further learned that evenly distributed modified $CaSO_4$ epoxy resin got better bonding performance of the interface epoxy resin in the interface area. Improved mechanical properties of modified $CaSO_4$ have broadened the application prospects in environmental engineering in terms of adhesive properties. Further exploration is needed to understand better and properly utilize $CaSO_4$ fillers.

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Conflicts of Interest

The authors declare no conflict of interest.

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