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Research Article

Synthesis of Starch Ether Grafted, Bio-Based Epoxy Resin and Their Impact on Mechanical Property

Tariq Aziz[1]*, Farman Ullah Khan[2], Roh Ullah[3], Fazal Haq[4] and Asmat Ullah5b[1]

[1]State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, China, Email: Tariq_mehsud@yahoo.com

[2]Department of Chemistry University of Science and Technology Bannu Pakistan, Email: farmandphil@yahoo.co

[3]College of Chemical and Biological Engineering, Beijing Institute of Technology (BIT), China, Email: Rohullah1@yahoo.com

[4]State Key Laboratory of Chemical 4Engineering, College of Chemical and Biological Engineering Zhejiang University, Hangzhou, 310027, China, Email: fhaq92@yahoo.com

[5]School of Pharmacy. Xi'an Jiaotong University, Email: Asmat_masood@yahoo.com

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***[1]Corresponding author:** Tariq Aziz, State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, China, Zhejiang University, Hangzhou, 310027, China, Email: Tariq_mehsud@yahoo.com

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Abstract

In the past decades, the epoxy resin has received extensive research interests and development particularly, in industrial fields, but with the passage of time and dramatic environmental changes, researchers are searching for the environmentally friendly bio-based epoxy resin. This provides us a new way for industrial as well as for our daily life. Herein, we report naturally occurring eugenol containing methylsiloxane and phenyl siloxane linkers having a separate chain measure. They have different liquid epoxy monomers having high purity. These silicone-bridged difunctional epoxy monomer having lower viscousness than commercial bisphenol A diglycidyl ether (DGEBA), epoxy with superior thermal properties, which were evaluated by thermal gravimetric depth psychology (TGA) and Scanning electron microscope (SEM). Starch ether was chemically modified by self-prepared bio-based epoxy resin. Bio-based epoxy clearly shows enhancement with the help of the modified amylum ether. Study urges a simpleton but productive chemical modification capability to sustainable interfacial adhesion composites properties.

This study shows a very easy and effective chemical modification of modified starch ether, to enhance interfacial adhesiveness composites with superior properties. Study their synthesis, structural morphological and thermal characterization of grafting copolymers with different ratios. Even though it's bending, and tensile performances are also showing good results, compared with the impact strength. We can say that our novel bio-based epoxy could form this process for further future research.

Keywords: Bio-based epoxy; Starch ether; Thermal properties; Adhesive properties

Introduction

Bio-based epoxy has unique properties with high stiffness and strong suit to weight ratio, relaxing feature, decreasing of crumbling, calm formation and short monetary use. These conditions make them essential, popular like other metals. Fiber-reinforced composites are vastly applied in leisure goods, automobiles, complex body parts etc. [1] Several promising results have been reported in the synthesis of bio-based epoxy resin using lingo-cellulosic biomass [2,3]. Resins and its derivate have the potentiality to cure epoxide soybean oil (ESO) without a significant decline of bio-based content. Maleopimaric acid (MPA) is one of the important derivatives of rosin which can be easily obtained by grafting an anhydride group [4]. A large amount of bio-based wage was used, for producing thermosetting medium such as resin and foam [5]. But still, it is a challenge to strengthen an epoxy resin by bio-based modifiers without trade wind-offs in its modulus, mechanical and thermal properties [6]. Therefore, nowadays the research worker and industrialist are emphasized towards such product which cannot harm the environment, as they have shown the favorable result in term of such impact [7]. As a result, bio-based polymer become considerably more attractive to their petrochemical-based counterparts, thermosetting polymers, vinyl ester (VE), and unsaturated polyester (UPE) resins have breakthrough utility in a large degree of industrial and display use as well as adhesion, coating and composition materials [8]. Generally, bio-

based polymers having intensity mechanical property such as low compressive strength, thermal stability due to their hydrophilic nature. However, by adding nanoparticles fillers in the bio-based polymer the mechanical, thermal and electrical properties should be greatly improved [9-11]. Therefore, renewable resources derived polymer (bio-based polymer) and their composites (bio-composites) have greatly attracted attention in recent years due to increased environmental concerns and intimate availability [12]. Many chemical products are prepared from oil-based monomers, bioethanol, and biobutanol as biofuels, biomass monomer-based such as polylactic acid and polyolefin are widely investigated [13]. Epoxy resins based on diglycidyl ether of bisphenol A have been used in industries for the thickness of matrices and composition materials, because of their excellent feature props properties such as high gear effectiveness, solvent resistance and efficient adhesion of various substrates [14].

Starch is a common, cheap and natural biopolymer and stunning prospect for animate strong filler for PLA [15]. Almost 11.3% of moldable plastic were prepared from starch-based compared with the aggregate moldable plastic used in the packaging area [16]. Starch derivate has used as a filler for hydrophobic polymers such as polyethylene to yield a partially bio-degradable polymer and also blended with a degradable polymer such as polyvinyl alcohol (PVA) and polycaprolactone (PCL), the addition of starch to PVA demonstrated improved tensile strength and elongation [17]. Crosslinking of starch improved its mechanical properties may be reliable possible to regular petroleum-based froth in agriculture and other industry [18].

The bio-based epoxy resin [19], self-prepared, used to analyze the mechanical properties of starch ether in this cogitation. Then the modified starch ether was coated on steel plates, magnify the interfacial adhesion between bio-based epoxy and steel plates. These synthesized liquid epoxy monomers with starch ether showing prevalent increase in mechanical properties. They are assuming to be favorable for the preparation of composites, with enhanced thermal and adhesive properties.

Materials and Methods

Materials

Starch ether with a noticeable density of 300-800CPS was supplied by Hangzhou color com Impex Co. Ltd (Zhejiang province China). Firstly, starch ether was dried at 75˚C for 16h to remove the moisture in a vacuumed oven. Then place it in sample glass bottle tightly covering their mouth. Bio-based epoxy was self-prepared in the state key laboratory. Reagents like ethanol and sodium hydroxide were obtained from the Aladdin reagent (Shanghai, China). All chemicals were used as received.

Modification of starch ether by bio-based epoxy resin

Modified starch ether was prepared in a three-necked round bottom flask having a thermometer and the mechanical stirrer. The round bottom flask was immersed in an oil bath having 80˚C. Starch ether with the amount of 20g and deionized water with 400mL was put into the flask for 2-3h with continuous stirring. Gelatinization when totally homogeneous, then 10wt. % of sodium hydroxide and 10wt. % of bio-based epoxy resin was put into the flask. Temperature increases up to 90˚C. Continuously Stirred up to 8h, the system was cooled, and then the mixture put into the petri dish cover with aluminum foil having small pores for drying in a hot air oven for 5-7h at 80˚C. After drying the liquid mixture, the obtained starch powder was washed with ethanol, passing 3 times, 15mins one round in centrifugation (Shanghai Anting scientific instrument factory), for 6-8h to remove the remaining sodium hydroxide and bio-based epoxy resin for further testing.

Steel plates preparation

The steel plate was polished with sandpaper, dried at room temperature, and then stored in a plastic bag, for further use.

Preparation of coated steel plates

A mixture of the bio-based epoxy resin 1g and starch ether with 1wt%, 3wt%, and 5wt% were taken in the sample glass bottle for 60min sonication, stirring for 30-45mins at 80˚C temps; and then stirred for another 15-20mins with deionized water, containing pH 2. Herein, 0.2g of triethylenetetramine TETA added as a curing agent and stirred with the next 10-15mins. After that, the product put into vacuumed oven maintaining 40˚C temps; for 5-10mins. After thorough stirring, the complete mixture was poured into four different samples for curing. Cured sample was carried out in a hot air oven at 120˚C for 1h. After that, the sample was cooled down at room temperature. These testing steel plates were placed 3-4 days before testing.

Characterizations

The structures of bio-based self-prepared epoxy resin, native and modified starch are checked for confirmation firstly by Fourier transform infrared spectroscopy FT-IR, spectrophotometer recorded on a Nicolet-5700 by the KBr-pellet method scanning from 4000-500cm^{-1} with a resolution superior to 0.5cm^{1}. The SEM figure was obtained on a scanning electron microscope (SEM, SU-8310) with X-ray spectrometer, covering of gold surface on the samples were applied. The analysis of the fracture surface images of native starch ether and modified-starch ether sized were obtained on this SEM. The thermal stability of the silane coupling agent (KH-560) under constant N_2 flow was studied by thermal gravimetric analysis TGA. Thermal degradation starting temperature (T0) 50°C, maximum decomposition temperature (T_{max}) 600°C and weight loss (%) are introduced. For adhesive properties, universal material testing machine (Zwick/Roell Z020 model) was used for such properties like tensile modulus and tensile strength were analyzed. Each measurement was repeated three times per sample, and the average was reported.

Results and Discussion

Chemical modification of starch

Self-prepared bio-based epoxy resin; native starch ether and modified starch ether are shown in Figure 1. The broad peak appeared at 3480cm^{-1} is due to –OH stretching vibration. The peak appeared at 2900cm^{-1} attributed to –CH stretching vibration. The

medium peak appeared at 730cm^{-1}assigned to -Si-C. The sharp peak at 2160cm^{-1} and medium peak at 1395cm^{-1} attributed to skeleton deformation vibration. The appearance of a peak at 1395cm^{-1} and the disappearance of the peak at 2160 cm^{-1} confirmed the successful synthesis of starch ether grafted bio-based epoxy resin [20-22].

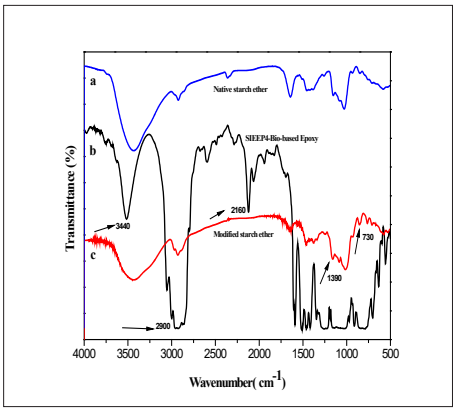

Figure 1: FT-IR spectra of (a) Native starch ether (b) Bio-based epoxy and (c) Modified starch ether.

Interfacial adhesion between starch ether and bio-based self-prepared epoxy resin

Bio-based epoxy resin property like interfacial adhesion shows significantly influence for durability. Fracture reinforced is analyzed showing changes in interfacial adhesion on steel plates when bio-based applied on modified starch ether. A large number of grooves having a smooth boundary is noticed at the fracture surface under SEM. After modification, the bio-based epoxy resin is strongly merged with one another. Different from the domestic starch ether, steel plates are dragged off a little portion with no gap, because of the typical characteristics difference between steel plates and bio-based resin. With the modification of starch ether, steel plates are well embedded in the bio-based epoxy. On the other hand, steel plate's surfaces are muffled with a layer of resin, which also indicated that after modification, interfacial adhesion of modified starch ether reinforced is improved. The interfacial adhesion between steel plates and the bio-based epoxy resin is in effect showing good inter-diffusion of the molecular layer between steel plates and bio-based epoxy [23,24].

Thermal gravimetric analysis of starch ether/bio-based epoxy resin

The thermal stability of the domestic starch ether and modified starch ether was investigated by using TGA, under constant N_2 flow. The main thermal parameters, including thermal degradation onset temperature (T_0), maximum decomposition temperature (T_{max}) and weight loss (%) are illustrated in Figure 2&3 (a) domestic starch ether show the highest thermal stability. This domestic starch ether material starts to decompose at 245-250˚C with 10% weight loss, and 340-350˚C with 35% weight loss and the maximum decomposition temperature are at from 360-450˚C 25% weight loss respectively. While on the other hand modified starch ether starts decomposes at 230-240˚C with 8% weight loss, and 310-320˚C 35% weight loss and from 420-430˚C 38% weight loss respectively [25,26].

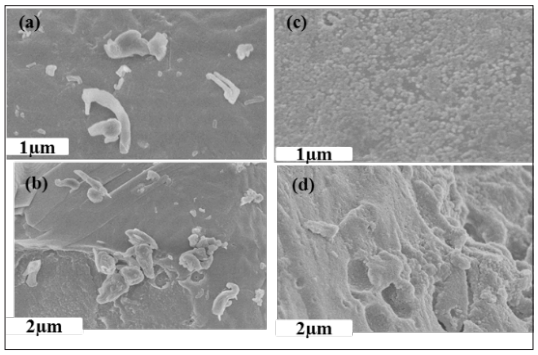

Figure 2: Fracture surfaces of (a, b) Native Starch ether and (c, d) Modified Starch ether.

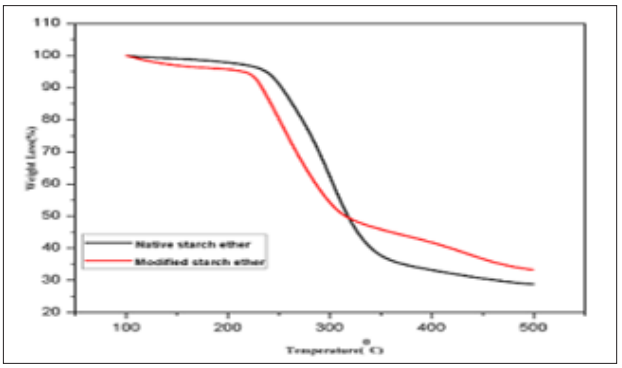

Figure 3: Starch ether and modified starch ether TGA.

Adhesive properties of starch ether with bio-based epoxy resins

Here the exact recipe to synthesize various kinds of polymers is described. The self-prepared bio-based epoxy resin was mixed firstly, with the calculated amount of triethylenetetramine TETA considered as a standard. A mixture of the bio-based epoxy resin 1 g and starch ether with 1wt%, 3wt%, and 5wt% were taken in the sample glass bottle for 60min sonication and after stirring for 30-45mins. Then 0.2g of triethylenetetramine TETA added as a curing agent and stirred with the next 10-15mins. After that the product put into vacuumed oven maintaining 40˚C temps; for 5-10 mins. After thorough stirring the complete mixture was poured into four different samples for curing After that, putting into the steel plates up to 1.5cm length and 2.4cm width, with the help of glass rod, first set of steel plates putting into the hot air oven for 1h up to 120˚C, containing 1wt % starch ether, second set containing 3wt % for 1h up to 120˚C and the third set containing 5wt % starch ether for 1h up to 120˚C starch ether for 1h to 120˚C. Sample plates, put it straight into the hot air oven, and for supporting, steel clips was used. After completion 1h the steel plates put out from the oven and placed it in room temperature removing the clips.

For bio-based epoxy, all the three moduli i.e. tensile, elongation and impact factors show greater enhancement and improvement in adhesive properties with starch ether as well as bending, tensile and impact strength was improved as shown in Figure 4, (a) the tensile strength increases by up to 20%, 15%, and 45%, from the standard of tensile strength. The bending strength of starch ether

with self-prepared bio-based epoxy shows an improvement of 13.8%, 13.5% and 15.8% separately, while the standard for bending strength is 10.3% compared with the pure bio-based separately. Moreover, the impact strength indicates a rise of 0.7%, 0.7%, and 1.1% while the standard for impact strength is 6.00% compared with the pure bio-based separately. Hence from the experimental study and analysis, it was clear that addition of modified starch ether with our self-prepared bio-based epoxy thoroughly and significantly increases the adhesive properties particularly using starch ether showing greater enhancement in all three parameters due to strong interfacial adhesion between steel plates with starch ether and bio-based epoxy [1,27,28].

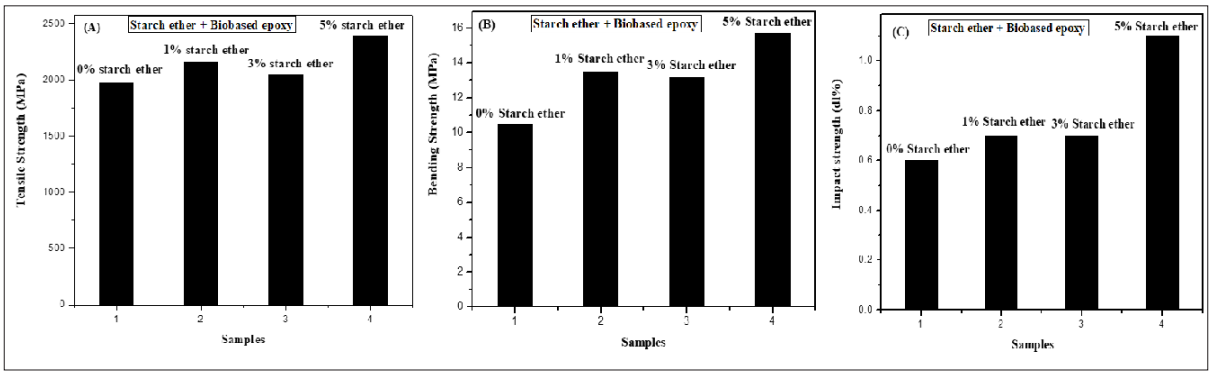

Figure 4: (a) Tensile strength (b) Bending strength and (c) Impact strength.

Conclusion

Improvement the interfacial adhesion between starch ether and bio-based an epoxy resin, a novel approach on modifying starch ether and enduing steel plates with superficial properties was successfully achieved by using self-prepared bio-based epoxy resin as the chemical modifier. Remarkable changes were noticed in all aspects especially using 5wt%, rather on 1wt % and 3wt % showing aggregation with our self-prepared bio-based epoxy matrix. Result revealed that self-prepared bio-based epoxy resin showing greater adhesive onto the starch ether with a chemical reaction which enhances and improve the interfacial adhesion between steel plates and bio-based epoxy. The overall adhesive properties, self-prepared bio-based epoxy composites enhance the orderly thermostability of bio-based epoxy resin. Composites study by SEM also confirmed that the modified sizing agent had an important effect on enhancing the interfacial adhesion between steel plates and bio-based epoxy. For more high performance, the sizing agent was an interpretative step. In short, in our study we used bio-based materials which are environmentally friendly and checked their physical properties, founding a dynamic and excellent improvement in adhesive properties. Bio-based epoxy shows enhancement with the help of the modified starch ether. The study suggested much more uncomplicated chemical modification method using sustainable interfacial adhesion with significant excellent properties.

Highlights

A. Starch ether reacted were a self-prepared bio-based epoxy resin.

B. Bio-based epoxy resin showed excellent improvement in adhesion property.

C. Our self-prepared bio-based epoxy has environmentally friendly.

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