Composites: Part A 105 (2018) 258–264

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

Reinforcement of economical and environment friendly Acacia catechu particles for the reduction of brittleness and curing temperature of polybenzoxazine thermosets

Abdul Qadeer Dayo [a,b], Rui-kun Ma [a], Sadia Kiran [a], Abdeldjalil Zegaoui [a], Wan-an Cai [a], Ahmer Hussain Shah [a], Jun Wang [a,*], Mehdi Derradji [a], Wen-bin Liu [a,*]

[a] Institute of Composite Materials, Key Laboratory of Superlight Material and Surface Technology of Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, PR China
[b] Department of Chemical Engineering, Balochistan University of Information Technology, Engineering and Management Sciences, Quetta 87300, Pakistan

ARTICLE INFO

Article history:
Received 1 October 2017
Received in revised form 29 November 2017
Accepted 2 December 2017
Available online 5 December 2017

Keywords:
Biocomposite
Thermosetting resin
Thermomechanical
Thermal analysis

ABSTRACT

The brittleness always remained a major concern for the polybenzoxazine thermosets. Several attempts have been made to overcome the brittleness issue, but all find some kind of sacrificing in other properties. A new and economical approach is presented by the reinforcement of catechin-rich Acacia catechu (AC) particles. The micro size AC particles blended with bisphenol-A aniline-based benzoxazine (BA-a) resin and isothermally cured. The terminal —OH groups of produced tannic acid participated in the curing process and helped in the ring opening of BA-a resin. The composites exhibited that the brittleness of polybenzoxazine has been improved by 35%, simultaneously its strength, Youngs' modulus, stiffness, glass transition temperature, and thermal stabilities are also enhanced. The highest impact strength of the composite is observed on only 4 wt% loading of AC particles and read as 5.2 ± 0.16 kJ/m^2, 307.1% higher than the value of neat poly(BA-a).

1. Introduction

In recent years, the increased environmental awareness, the depletion of petroleum reserves, and the global approach towards the sustainable development have raised the interest of both academia and industries towards the production of environmentally sustainable products. The production of chemicals and products partially or fully by using the bio-based sustainable feedstock is nowadays a real challenge. In this context, some investigators have utilized bio-based sustainable feedstock as an efficient modifier for thermosets. The bio-based materials have been successfully applied in building, automobiles, aeronautics, furniture, and naval application. In addition, natural fillers also have a number of fascinating properties like their low cost, ease of processing, and lower abrasiveness during processing, which encourage their use as reinforcing agents for polymer matrices [1–3]. The produced composites are commonly cheap as compare to the pristine polymer having minimal impact on the environment and have better mechanical and thermal properties compared to those pristine matrices.

Polybenzoxazine resins are novel types of phenolic resins with molecular design flexibility and high strength properties as compare to traditional phenolic and epoxy resins. Polybenzoxazine has been reported with appealing properties such as excellent mechanical and thermal properties, high resistance to heat and chemicals, low melt viscosities, lower flammability, near-zero volumetric change on curing, and low dielectric constant [4–8]. Due to these appealing properties, they are applied in a wide range of applications such as structural composites, coatings, adhesives, and electronic materials. However, the higher curing temperature and brittleness are the major associated disadvantages of polybenzoxazines resins [8]. Therefore, they are withdrawn from various fields especially when lower curing temperature and higher toughness properties are desired for the product. Several methods are applied to reduce the curing temperature of polybenzoxazines, but blending with phenolic compounds rich substances were observed as best and economical. The curing temperature studies showed that the blending of benzoxazine monomers with cashew nut shell liquid [9,10], hemp fibre [11,12], chitosan [13], and crab shell particles [14] greatly reduced the energy requirement.

* Corresponding authors.
E-mail addresses: wj6267@sina.com (J. Wang), wjlwb@163.com (W.-b. Liu).

https://doi.org/10.1016/j.compositesa.2017.12.004
1359-835X/

Moreover, the higher toughness was recorded for the polybenzoxazine composites/alloys after the addition of hyperbranched polymers [15], rubber [16,17], chitosan [13], crab shell particles [14], carbon nanotubes (CNTs) [18], and clay [19,20] in the neat polybenzoxazine. Though these approaches have reduced the brittleness and curing temperature, while, decline was also recorded in other properties like thermomechanical, mechanical, and thermal properties. In addition, the key problem was the addition of a higher amount of modifier for the reduction of and curing temperature and brittleness.

Acacia catechu (AC) bark is a polyphenol-based red tea rich in tannins [21], obtained from a fugacious tree found in South Asia, mostly in China and India [22]. The excellent anti-inflammation and anti-cancer activities were observed in the AC due to the presence of tannins [23]. It has been used as a natural dye or a mordant for the textile industries [24,25]. The catechin and epicatechin flavanol monomers are the main constitutes of the AC, they produce tannins on the polymerization reaction [26–28]. The AC treated flax fibre composites showed improvement in the mechanical properties [29]. The polyphenols extract from green tea is also reported as a material for the enhancement of mechanical and thermal properties [30].

In the current study, the AC powder, as a novel reinforcement material, was loaded in bisphenol-A aniline-based benzoxazine (BA-a) monomer, without the addition of any solvent. The blends were characterized for the curing behaviour, tensile, and impact studies and the results were compared with the pristine polymer. In addition, thermomechanical properties and thermal stabilities are also analyzed. Moreover, the tensile test fracture surfaces of the neat polymer and AC filled composites were also studied.

2. Materials and methodology

2.1. Materials

The traditional BA-a monomer was kindly gifted by the Jiangxi Huacui Advanced Materials Co., Ltd. (China). AC powder was purchased from the local vendor in Harbin, China. All the reagents were supplied by Shanghai Jingchun Reagent Co., Ltd. (China) and used as-received.

2.2. Sizing of AC particles

The received AC was ground in a planetary ball-mill (pulverisette 7, FRITSCH) in a ZrO_2 vessel at a speed of 300 rpm for 3 h; ball-to-material weight was maintained at 15:1. Grinded AC was sieved by using a vibrating sieve shaker, and collected particles on 500 mesh (Tyler sieve standard) were used in the study. A statistical study of the AC particles dimension was performed and the obtained results, presented in Fig. 1, revealed an average particles size of 4.5 μm.

2.3. Curing of AC containing benzoxazine composites

The desired mass amount (1, 2, 3, 4, and 5 wt% (wt%)) of AC powder and 25 g of BA-a monomer were added in a flask and then melted on the melting apparatus. For the better dispersion of AC particles, the mixture was stirred at 90 °C for 15 min. The embedded gases can increase the voids in the final cured samples, so the solution was degassed in a vacuum oven at 100 °C for 6 h. After that, the degassed solution was transferred into a stainless steel mould having required test dimensions and cured in an air-circulating oven at 150, 160, 170, and 180 °C for 1.5 h at each heating stage. The neat polymer was also prepared following the same procedure. The specimen was coded as BA-a/ACX and P(BA-a/ACX) for the uncured and their cured specimen, respectively, and X represents the wt% of AC added to the matrix.

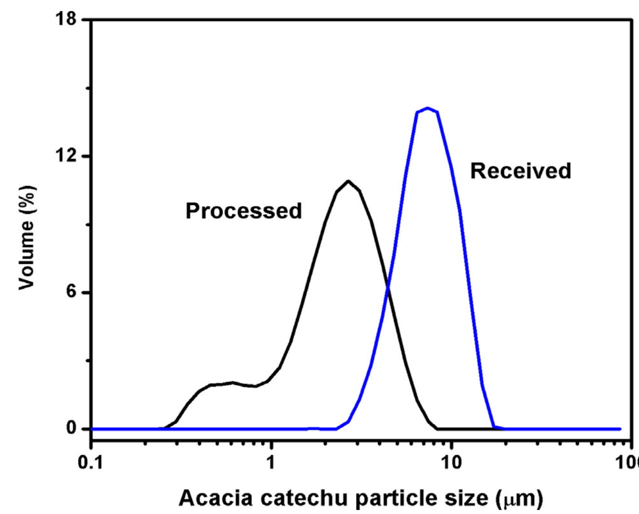

Fig. 1. Size distribution of received and processed Acacia catechu particles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.4. Characterizations

Calorimetric analyses were carried out on a differential scanning calorimetry (DSC) unit; model Q200 of TA Instruments, USA. The ~5 mg weight of the sample was placed in aluminium pan under nitrogen atmosphere and characterized from 30 to 350 °C at 20 °C/min. The tensile tests were recorded on Instron 5569 at 1 mm/min crosshead speed; specimen size was about 50 × 10 × 2 mm^3, whereas, ASTM D256-2010 standard was followed for the Izod impact test on Tinius-Olsen impact device. The rectangular specimen of 63.5 × 12.7 × 3.2 mm^3 was notched at 45°, five samples were tested and mean value of absorbed energy was reported. The thermomechanical properties of neat polymer and composites were determined by a dynamic mechanical analyzer (DMA) model Q800, TA Instruments (USA). A rectangular sample was tested in the single cantilever mode and 1 Hz frequency with a 3 °C/min heating ramp from 40 to 240 °C under a nitrogen atmosphere. The thermal stabilities of the AC particles, neat polymer and composites specimens were studied under 50 mL/min of nitrogen (N_2) purging by using a Q50 (TA Instruments, USA) at a 20 °C/min heating rate from 50 to 820 °C. The morphology of tensile test fracture surfaces in corresponding samples was investigated by scanning electron microscope (SEM), CamScan MX 2600FE, Oxford Instruments, UK, at 20 kV accelerating voltage.

3. Results and discussion

3.1. Effects of AC loading on the curing behaviour

The influence of AC content on the curing behaviour of BA-a monomer was studied by the DSC analysis. The curing behaviour is one of the important parameters for the thermosets resin. The DSC analysis curves of uncured neat BA-a monomer and blends of BA-a monomer with different AC wt% loadings are presented in Fig. 2, and parameters are summarized in Table 1.

We would see from the DSC exothermic curves of neat BA-a monomer and BA-a/AC blends that the curing process was much affected by the addition of AC particles. The decline was recorded in the curing exotherm peak temperature (T_p) as well as the initial