Materials Letters 197 (2017) 31–34

Contents lists available at ScienceDirect

Materials Letters

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

Polymer-coal composite as a novel plastic material

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ARTICLE INFO

Article history:
Received 28 January 2017
Received in revised form 21 March 2017
Accepted 26 March 2017
Available online 27 March 2017

Keywords:
Composite polymeric material
Polyvinyl alcohol
Coal
Carboxymethyl starch
Degradable plastic

ABSTRACT

Novel composite polymeric material was prepared from coal, carboxymethyl starch (CMS) and polyvinyl alcohol (PVA). Coal was first treated with NaOH to partially dissolve the coal into sodium humate (SH) and the SH along with undissolved residue was blended with CMS and PVA solution to prepare a polymeric composite though hydrogen bonding. The composite materials showed tensile strength in the range of 8–10 MPa for potential applications including plastic bags and films. The residue after coal dissolution in NaOH served as filler while the SH led to bonding with CMS/PVA in water though hydrogen bonds as detected by Fourier Transform Infrared (FTIR) spectroscopy and X-ray Photoelectron Spectroscopy (XPS).

1. Introduction

Coal has been used as a feedstock in the production of a wide range of chemicals and materials [1]. To produce chemicals such as methanol, hydrogen and carbon monoxide coal is first transformed to syngas. From these precursors, high-value added products are manufactured [2,3]. Although, this type of coal utilization has been done technically and economically for many decades [4], it's energy efficiency is very low, and it is environmentally unfriendly due to carbon and other emissions [5–8]. Therefore, it is of great importance to use coal directly in the manufacture of materials with little or no pollution.

Preparation of polymeric composite materials from coal is one way to directly use coal. Prior research has been mainly focused on blending coal and polymers to improve the thermal stability, mechanical strength and electrical conductivity of polymers [9–11]. In the above composites, coal played the role of filler but the coal particles could not be strongly bonded with polymer.

Therefore, the objective of this research was to find a facile method to directly utilize coal to prepare materials. There are many hydrogen-bonds in the molecules of coal, especially in low ranked or weathered coals, which could be broken and could be bonded with polymers to make new materials. Here, we developed a new composite material through hydrogen bonding of coal and polymer.

2. Experimental

2.1. Materials and methods

A weathered coal from Wuhai City, China was used to prepare composite polymeric material. Coal analyses using Chinese standard methods [12,13] showed 64.92, 28.27, 4.00, 1.51 and 1.30% of C, O, H, S and N contents, respectively. First, coal was ground into fine powder and sieved to obtain <75 μm particles. The reagents used in this study were as follows: Analytical reagent (AR) grade PVA was obtained from Beijing Organic Chemical Plant, sodium hydroxide and hydrochloric acid, both AR grade were obtained from Shanghai Suyi Chemical Plant and Na CMS of pharmaceutical grade was procured from Baoding Shenghui Polymer Plant.

Sodium hydroxide was selected to extract humic acid (HA) as SH by partially dissolving the coal. CMS and PVA were selected as the flexible polymer matrix, which is expected to easily form hydrogen bonds between coal and polymers. Coal, PVA, CMS, NaOH and deionized water were put into a flask and heated at 60 °C in a water bath while stirring. The different components were varied to optimize the materials. The reaction between these components was stopped at different time intervals and the mixture was poured onto the surface of a large horizontal glass plate to make a plastic film at room temperature upon drying. The PVA/CMS ratio was fixed at 1:1 while the ratio of coal to PVA/CMS was varied. The role of coal particle size on the tensile strength of films was also investigated.

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http://dx.doi.org/10.1016/j.matlet.2017.03.148
0167-577X/

2.2. Characterization

A universal tester machine from Jinan Hensgrand Instrument Co. (LDS-02) was used to measure tensile strength and percentage of elongation on five replicates of films. The film morphology and thickness were investigated by scanning electron microscopy (SEM) using a Quanta 250 instrument. Three-dimensional shapes of the films were further measured by atomic Force Microscopy (AFM) using Bruker Dimension Icon equipment. Samples were also characterized by FTIR spectroscopy using a Bruker VERTEX 80v IR spectrometer. Thermal gravimetric (TG) and differential thermal gravimetric (DTG) analyses were carried out using a thermal analyzer, STA 780 (Stanton Redcroft, England). The samples were heated from 25 to 350 °C at a constant rate of 10 °C/min, but kept at 110 °C for ten minutes for removing water from the plastic films. XPS investigations were performed on films with ESCALAB 250Xi (Thermo Fisher Scientific) electron spectrometer.

3. Results and discussion

3.1. Morphology of plastic films

New polymeric material was made into black plastic film as can be seen from Fig. 1A. The film was black because of black coal particles. The as-prepared films were flexible and could be translucent . SEM images of the three different films made by adding different amounts of coal are shown in Fig. 1B–D.

The plastic film formed only by PVA/CMS has many pores and cracks (see Fig. 1B and its inset) as a result of shrinkage upon drying. After 30 and 40 parts by weight of weathered coal were added, pores and cracks disappeared from the surface of film (Fig. 1C and D and their insets) because of little or no shrinkage due to the bonding of coal particles (filler) to the polymer. This result suggested that the coal particles, SH and PVA/CMS were compatible and bonded together. The particles of partially dissolved coal solid were uniformly dispersed in the film as can be seen from Fig. 1C and D. Coherent films along with the uniformly dispersed particles of coal residue could also be seen in AFM images (see insets of Fig. 1C and D). When more coal (40 parts by weight) was added into the film, its surface was still smooth with coal particles evenly aligned (Fig. 1D and inset), even though there are too many insoluble coal particles in the film. The sizes and amount of coal particles, might determine the tensile strength and breaking elongation of plastic films (see below).

3.2. Mechanical properties

Tensile strength and breaking elongation length were measured (Fig. 2). The higher the breaking elongation length, the greater is the toughness. Fig. 2a shows that the tensile strength of films increased with increasing coal content, while breaking elongation increased first and then decreased. The above increased tensile strength and breaking elongation indicated that the SH had strong interaction with PVA/CMS. If SH had no interaction with PVA/CMS, the coal would have played the role of rigid particles, which would have improved tensile strength but decreased the breaking elongation. Here, the breaking elongation increased first because of the strong interaction of SH with PVA/CMS, which was more than the reduction that could be caused by the rigid coal particles. With PVA/CMS amount constant, the strength of H bonding gradually reached saturation but then diminished with increasing coal content. The maximum value of breaking elongation was obtained with 30% coal content (Fig. 2a). The particles of residue not only served as filler but also served as reinforcement to increase toughness while the SH interacted and bonded with PVA/CMS leading to good strength (Fig. 2a). The strong interaction of SH with PVA/CMS is based on strong bonding through large number of hydrogen bonds (see below).

In addition to the above effect of coal content on strength (Fig. 2a), the influence of the particle sizes of weathered coals on mechanical properties (Fig. 2b) was also investigated. As the particle size of coal decreased, the tensile strength and breaking

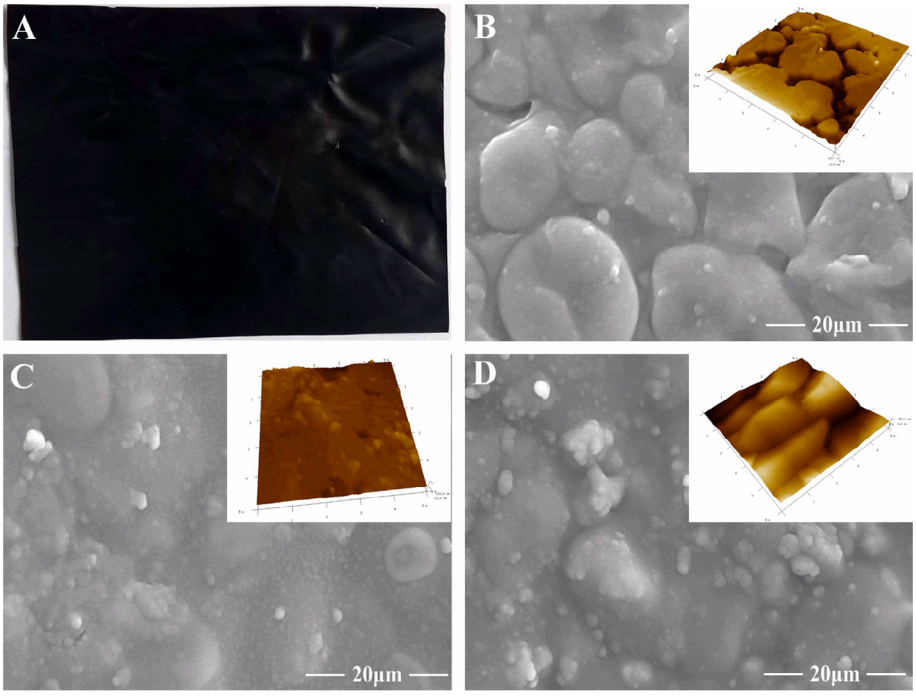

Fig. 1. Photograph of film made from PVA + CMS (1:1), coal, NaOH and water with 100, 30, 8 and 330 parts by weight, respectively (A), SEM micrographs of composite films, all made from PVA + CMS (1:1), coal (x), NaOH and water with 100, x, 8 and 330 parts by weight, respectively but with different parts by weight (x = 0, 30 or 40) of coal: (B) Coal 0 parts, (C) Coal 30 parts and (D) Coal 40 parts. Insets of B, C and D are AFM images.