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Effects of cellulose, hemicellulose, and lignin on the morphology and mechanical properties of metakaolin-based geopolymer

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HIGHLIGHTS

- Alkaline degradation of hemicellulose was found in FTIR.
- Hemicellulose resulted in insufficient geopolymerization detected in SEM.
- Lignin led to the porous morphology and brittle fracture of geopolymer.
- Cellulose fibres caused the dense structure and ductile failure of geopolymer.
- Good bonding was detected between cellulose fibres and geopolymer matrix.

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ABSTRACT

Natural fiber-reinforced geopolymer has attracted wide attention in construction and building materials due to its low cost, low density, and excellent mechanical properties. Cellulose, hemicellulose, and lignin are the three basic components of natural fibres, and were investigated to reveal their influence on the metakaolin-based geopolymer. Comparative evaluations were investigated via morphology analysis and mechanical strength analysis. The results showed distinct microstructures and mechanical properties of the geopolymer-based materials with cellulose, hemicellulose, and lignin, respectively. A low content (5 wt%) of lignin, cellulose, and hemicellulose enhanced the flexural and compressive strength of pure geopolymer. Higher lignin and hemicellulose led to the porous morphology, lower density, and brittle fractures of geopolymer-based composites, which reduced the flexural and compressive strength in these geopolymer-based composites. It was noted that the degree of geopolymerization was clearly lowered by the alkaline degradation of hemicellulose. With the increase in cellulose content, in contrast, the denser structure and fewer pores of the geopolymer matrix were detected, as well as ductile failures of geopolymer-based composites. Good bonding was also shown between the geopolymer matrix and cellulose fibres without remarkable degradation. The results of this study will facilitate a better understanding of the effect of lignocellulosic biomass in natural fibre-reinforced geopolymers and should serve as the basis for further research and applications.

1. Introduction

Geopolymer, by reduction of CO_2 emissions, has emerged as an environmentally friendly alternative to Portland cement thanks to its high compressive strength, low shrinkage and creep abilities, excellent inflammability, and exemplary durability [1–5]. Thus, geopolymer can be used in a wide range of applications, such as civil infrastructure (roads and railways), sustainable construction and building materials, and specific industrial applications (radioactive immobilization and contaminant encapsulation) [6–10]. However, like most ceramics, pure geopolymer suffers from brittleness problems, which can be overcome with fibre reinforcement in the geopolymer matrix [11,12].

Growing attention to environment and climate change has piqued people's interest in natural material production and environmental protection materials. It is generally recognized that natural fibres derived from wood, bamboo, cotton, flax, etc. [12–15] have been widely applied to reinforce the geopolymer matrix or to produce lignocellulosic biomass-based materials with geopolymer binders due to these fibres' advantages with regard to natural

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abundance, recyclability, low cost, low density, excellent mechanical properties, and nontoxicity [16,17].

Many previous studies dealt with natural fibres as a unit. In fact, natural fibre, in terms of chemistry, is a biopolymer composite composed mainly of a network of cellulose (40–60 wt%), hemicelluloses (20–40 wt%), and lignin (10–25 wt%) [18,19]. The content of these three chemical components in several natural fibres [20–23] is listed in Table 1. As shown, cellulose, hemicellulose, and lignin are the major components of natural fibres (72.3–99.5 wt%), albeit in quite different lignocellulosic biomass from one species to another. If the different effects of cellulose, hemicellulose, and lignin on geopolymer can be found, it will be possible to better understand the bonding mechanism between natural fibres and geopolymer, and to choose which natural fibre is best suited to the development of natural fibre-reinforced geopolymer composites.

The objective of this work was to investigate the influence of the common chemical composition of natural fibres, especially cellulose, hemicellulose, and lignin, on geopolymer properties. Comparative evaluations were investigated via morphology analysis and mechanical strength (flexural and compressive strength) analysis. The results of this study will facilitate improved understanding of the lignocellulosic biomass in natural fibre-reinforced geopolymers to serve as the basis for further research and applications.

2. Materials and methods

2.1. Materials

High purity grade cellulose fibres (medium), hemicellulose (xylan), and lignin were supplied by Sigma (St Louis, MO, USA). A commercial metakaolin (MK) (Metamax®, BASF, Germany) was used as the aluminosilicate source. The chemical compositions of MK were measured by X-ray fluorescence (XRF) (XRF-1800, Shimadzu, Japan), the results of which are presented in Table 2. The particle size distribution (PSD) of MK (dispersed in water) was assessed with a Mastersizer 2000 particle size laser analyzer (Malvern Instruments Ltd, Malvern, UK). The values of the PSD of MK, d_{10}, d_{50}, and d_{90} were 1.120 μm, 4.120 μm, and 12.966 μm, respectively.

2.2. Activator solution

The activator solution for geopolymerization was made by mixing analytical grade sodium hydroxide (NaOH) with sodium silicate (Na_2SiO_3) (Wuxi Yateks Joint Chemical Industry Co., Ltd., Jiangsu, China). The volume ratio of Na_2SiO_3/NaOH was 2.5. The molar ratio (SiO_2/Na_2O) of the activator solution was maintained at a value of 1.33 using 10 M NaOH.

2.3. Composite preparation

Different contents of cellulose, hemicellulose, and lignin (5 wt%, 10 wt%, or 20 wt%) were mixed with MK. An activator solution was then added to the mixture to obtain the mortars. The mortars were stirred and cast onto open Teflon molds at an ambient temperature before curing under different conditions: ambient temperature for group G, and dried at 80 °C for 48 h for group GH (preheating treatment), respectively. Specimens were then cured for 7 days at room temperature before testing. The codes of the specimens are listed in Table 3.

2.4. Characterization

2.4.1. Fourier transform infrared (FTIR) spectroscopy

The dry samples (10 mg) were dispersed in a matrix of KBr (70 mg), followed by compression at 12 MPa for 2 min before being tested with a Vertex 70 FTIR spectrophotometer (Bruker, Ettlingen, Germany) in the spectral range from 4000 to 400 cm^{-1}.

2.4.2. Scanning electron microscopy (SEM)

The cross-sectional microstructures of the fracture surfaces of the composite specimens were tested after flexural testing. Micro-images of the geopolymer-based composites coated with gold were examined via SEM (Quanta FEG 250, FEI, Eindhoven, Netherlands) at 10 kV.

2.4.3. Mechanical tests

The densities of the specimens were calculated before the mechanical tests, and the results for each specimen were the average of at least three repeated tests. Three-point bend tests were used to evaluate the flexural strength (80 mm × 20 mm × 10 mm) with Instron 3365 Universal Testing Machine (Instron, Norwood, MA, USA) at a speed of 1 mm/min and a specimen span of 64 mm. All flexural tests per sample were repeated more than five times, and the average values were reported. The compressive strength (30 mm × 20 mm × 10 mm) was determined using a MMW-50 mechanical testing machine (Jinan Resistance Test Machine Co., Ltd., Shandong, China) at an applied speed of 1 mm/min. The average values of compressive strength for each sample were obtained by repeating the test at least three times.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectra of the geopolymer-based composites are displayed in Fig. 1. The wide vibration bands around 3500 cm^{-1} and 1652 cm^{-1} exhibited in all spectra were attributed to O–H stretching and bending, respectively [24–26]. The intensity of the peaks at 451 cm^{-1} was associated with Si-O-Si bending vibration [27]. Another intense band was centered around 1020 cm^{-1}, corresponding to the Si-O-Al and Si-O-Si vibration bands of the geopolymer. In addition, the chemical composition of natural fibres in all geopolymer-based composites were represented in the peaks at 2912 cm^{-1} and 1460 cm^{-1}, corresponding to the alkane CH stretching vibrations of the methylene groups as well as the CH_3 asymmetric deformation vibrations or CH_2 scissor vibrations [28,29]. Notably, the peak around 1610 cm^{-1} of carboxylate anion (COO^-) was detected in G-H20, indicating ionization of carboxylic acids due to the alkaline degradation of hemicellulose [30,31].

Table 1
Content of cellulose, hemicellulose, and lignin in several natural fibres.

Natural fibre	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Total (wt%)
Cotton	89.7	1.0	2.7	93.4
Flax	80	13	2	95
Hemp	74.1	7.6	2.2	83.9
Sugar cane	51.8	27.6	10.7	90.1
Bamboo	54.6	11.4	21.7	87.7
Coconut	51.3	11.7	30.7	93.7
Wheat straw	38	36	22	96
	38.0	29.0	15.0	82
	33.2	24.0	15.1	72.3
	28.8	39.1	18.6	86.5
Rape straw	36	37	24	97
	37.6	31.4	21.3	90.3
Spruce + bark	42	27	26	95
	41.0	24.3	30.0	95.3
	50.8	21.2	27.5	99.5
Poplar wood	50	30	≤20	≤100