Modification and Properties of EVA Foamed Material with Hemp Stem Powder

Yafei Guo, Xinmin Hao*, Gaoyong Liang
Quartermaster Engineering Technology Institute, Beijing, China
email: guoyafei1010@jnsys.onexmail.com
*email: xinmhao@jnsys.onexmail.com

Abstract. In this study, a certain amount of hemp stem powder was added into ethylene-vinyl acetate (EVA) copolymer foam system by molding, and the improvement of properties of composite foam system with different hemp stem powder content of 0-30% was studied. The results showed that hemp could decrease the hardness and density of the composite foam system, improve the resilience and compression deformation rate, and have excellent moisture absorption and quick drying properties and antibacterial properties. The results show that the foaming system with 10% - 20% hemp stem powder has the best comprehensive mechanical properties, which can be used in shoes.

1. Introduction
EVA (ethylene vinyl acetate copolymer) foam material is light, soft, good resilience, chemical corrosion resistance, and relatively low price. It is widely used in the soles and insoles of sports shoes, absorbing the impact force generated in sports, providing protection and relatively mild feeling. EVA products will be found in almost every sports shoes brand. However, the mechanical properties of single EVA foam materials often can not meet the requirements of daily use. In order to improve the performance, different modifiers are usually added for composite foaming. The common research focuses on the modified foaming materials such as starch and wood flour [1-3]. There are few reports on the preparation of foaming materials by EVA modified with hemp stem powder [4].

Hemp stem powder is the core fiber of hemp stalk after the removal of bast fiber, accounting for 60% - 80% of the total proportion of hemp stalk. And the density is about 0.28-0.44g/cm³, which is lower than the density of common wood flour. It is mostly used as straw combustion, with low economic benefit and environmental pollution. The research shows that, hemp stem surface has a large number of hydroxyl and connected pores which infers large specific surface area, that is conducive to the absorption and volatilization of moisture[5-6]. Meanwhile, hemp stem powder is a natural antibacterial agent. Studies show that hemp core powder and its blended fabric have excellent antibacterial properties against Staphylococcus aureus, Escherichia coli, Candida albicans, etc. [7-10]. In this study, hemp stem powder was introduced into EVA foam system to improve the mechanical properties of EVA foam material [11-12], and give the foaming composite excellent moisture absorption and quick drying properties and antibacterial properties. Moreover, the process is simple, the cost is low, and the application prospect is broad.
2. Experimental materials and methods

2.1. Experimental materials and instruments

cEVA, with mass percent of vinyl acetate is 25%, was provided by Taichang Yusheng Shoes Co.Ltd. High temperature foaming agent AC3000, was provided by Hangzhou Haihong chemical Co.Ltd. Cross linking agent DCP, was provided by coin Akzo Nobel peroxidespte . Zinc oxide was used as foaming auxiliary agent and stearic acid was used as mould release agents for this study. Both of them are purchased industrial grade goods. Self-made hemp stem powder partical size is 10-40μ m with uniform dispersion.

2.2. Preparation of modified foaming materials

2.2.1. Mixing

When EVA and hemp stem powder were mixed as mixture A, the mass percentage of hemp stem powder was 0%, 10%, 20%, 30% and 35%, respectively. The foaming agent, crosslinking agent and foaming agent were mixed as mixture B in a certain proportion. Added the mixture A into the mixer when the temperature of the inner chamber of the mixer is heated to 80 °C for mixing. The first dedusting is conducted at 95 °C, the second dedusting and turning is conducted at 100 °C, and the third dedusting is conducted at 105 °C. After mixing for 15 minutes, The mixture B was added into the mixer for the fourth dedusting and turning. Continue mixing for 3 minutes with the rotating speed is 30rpm. The resulting copolymer was used as mixture C.

2.2.2. Cutting

After mixing, the mixture C was added into a five roller open mill, and pressed into thin sheets with a thickness of 1.5 mm, which are cooled at room temperature and then cutted.

2.2.3. Foaming.

The temperature of the mold built in the foaming machine was heated to 160 °C, and then the release agent was sprayed uniformly. The mixture C was added into the mold to molded foam for 650s as the molding temperature was 160 °C, and molding pressure was 15 MPa.

2.2.4. Demoulding

After foaming, release the pressure and hop the mode. The foaming composites were obtained by cutting the foaming materials into 20 * 18cm rectangular blocks. the foaming samples were named as EVA0, EVA1, EVA2, EVA3 and EVA4, as the hemp stem powder mass content was 0%, 10%, 20%, 30% and 35%, respectively.

2.3. Testing and characterization

The properties of EVA0, EVA1, EVA2, EVA3 and EVA4 were tested and characterized respectively.

2.3.1. Structural Characterization

The internal pore structure of the foaming composite was observed by JSM-6360 scanning electron microscope. IR spectra of the foam material were collected and analyzed by Thermo Scientific Nicolet IS20 Fourier transform infrared spectrometer.

2.3.2. Mechanical Properties

The mechanical properties of the composite foamed materials were characterized according to the relevant national standard test methods. The hardness was tested according to HG-T 2489-2007, the density was tested according to GB/T 6343-2009, the resilience was tested according to GB/T 10652-2001, and the compression deformation rate was tested according to HG-T 2876-2009.
2.3.3. Moisture Absorption and Quick Drying Properties.
According to GB/T 9995-1997, the moisture regain of the samples was tested. All the samples were soaked in distilled water for 24 hours to test the saturated water absorption, which was used to characterize the moisture absorption capacity of the samples., and The moisture release percentage of the samples were used to characterize the fast drying ability while controlling the water carrying rate of all samples to 6%.

2.3.4. Antibacterial Properties.
According to QB/T 2881-2013, the antibacterial properties of insoles made of foaming composite before washing and after washing for 15 times were tested. The human trial wearing experiment were also organized.

3. Results and discussions

3.1. Analysis of Structure and morphology

The SEM images of EVA foamed materials with different hemp stem power contents (0, 10%, 20%, 30%, 35%) are shown in Fig. 1. It can be seen that with the increase of hemp content, the foaming degree is gradually improved, and the uniformity of cell is improved. This may be due to the HSP dispersed in the matrix and promoted the heterogeneous nucleation. When the content of foaming agent is fixed, the content of gas used for foaming is constant, while the nucleation point increases due to heterogeneous nucleation, therefore, the cell size decreases. The addition of hemp stem power improves the melt strength of the matrix, inhibits the cell growth, reduces the cell merging phenomenon caused by cell rupture. As a result, the cell size was reduced and homogenized. However, when the content of hemp is more than 20%, the dispersion of hemp becomes poor, which is easy to cause agglomeration, resulting in the decrease of cell size uniformity. Interestingly, we have observed some phenomena in hemp stem power modified EVA foam, which are different from those of EVA foam material, as can be seen in Fig 2. Fig 2(a) shows that there are wrinkles similar to spring structure on the cell wall. This unique structure may be an important factor to improve the mechanical properties of the composite, which will be discussed in the following chapters.
Figure 3 shows the IR spectra of hemp and different EVA samples. Fig 3 curves show that the carbonyl group in hemp vibrates at 1734.91 cm$^{-1}$, forming the characteristic peak. However, there is no characteristic peak in the infrared detection of EVA material without adding hemp stem powder. With the addition of hemp, all of the EVA foam composites show the characteristic peak, which indicates that the hemp has been successfully added to the foaming system.

3.2. Analysis of mechanical properties

Table 1 shows the test results of density, hardness, compression deformation rate and rebound rate of EVA composite foam materials with different hemp stem powder content. The data in the table indicate that with the addition of hemp, the mechanical properties of the composite foam materials are obviously improved. The density decreases by 23.7%-34.6%, the hardness decreases by about 28%, the rebound rate increases by 13%-21%, and the compression deformation rate increases by 31.6%-42.6%. This change is consistent with the structural change observed in SEM images (Fig. 1). The increase of the number of bubbles helps to reduce the density and hardness of the material, so as to be more portable. With the addition of hemp stem powder, wrinkles like spring structure are observed inside the hole (as shown in Fig. 2(a)). It can be considered that this kind of wrinkle helps to improve the resilience and compression deformation rate of the materials. The composite can absorb more energy when under stress, thus improving its protection function and wearing comfort. When the content of hemp is 35%, the resilience and compression deformation rate begin to decrease, which can be explained by the weakening cell structure in Fig. 1(e).

| Samples | Density (g/cm$^3$) | Hardness (C) | Compression deformation rate (%) | Resilience (%) |
|---------|--------------------|--------------|----------------------------------|----------------|
| EVA0    | 0.156              | 50           | 23.70                            | 38.00          |
| EVA1    | 0.102              | 36           | 31.40                            | 45.00          |
| EVA2    | 0.107              | 36           | 33.80                            | 45.00          |
| EVA3    | 0.102              | 37           | 33.20                            | 46.00          |
| EVA4    | 0.119              | 37           | 31.20                            | 43.00          |
3.3. Analysis of Moisture Absorption and Quick Drying Properties

Figure 4 Moisture adsorption curve of EVA samples

Figure 5 Moisture liberation curve of EVA samples

The test results of moisture absorption and quick drying performance of EVA samples are shown in Fig. 4 and Fig. 5. With the increase of hemp content, the water absorption of the composite foam material increases at first and then decreases. This is partly due to the existence of large amounts of hydroxyl in hemp, which can form hydrogen bond with free water molecules and enhance the adsorption of water. Therefore, the composite foam materials can absorb more water. In addition, the cell size is also an important factor affecting the water absorption of the material. The larger the cell size is, the more water molecules it can hold, and the greater the saturation water absorption of the material. It can be seen from Figure 1 that when the content of hemp is greater than 20%, the dimensional stability of the cell becomes worse, which leads to the decrease of water absorption. It can be seen from the moisture liberation curves in Fig. 5 that the moisture release rate of the composites with hemp stem powder is significantly higher than that of EVA foam. In the same drying time, EVA foaming composite with hemp content of 10% has the fastest moisture release rate.

3.4. Analysis of antibacterial Properties

According to the national military standard test method, the antibacterial property of the insole made of composite foam material was tested. Before washing, the antibacterial rate of insole to Staphylococcus aureus and Klebsiella pneumoniae was 99%, and to Candida albicans was 94%. After washing for 15 times, the antibacterial rate only decreased slightly. The antibacterial rate to Staphylococcus aureus, Klebsiella pneumoniae and Candida albicans was 98%, 98% and 88%, respectively. The antibacterial rate before and after washing was higher than the national standard value, especially the antibacterial rate of Candida albicans after washing was 25.7% higher than the standard value. In addition, the research team also carried out a human trial on the application performance of the composite foam material. See reference 8-9 for details. After data analysis of 214 people who try on the shoes, it is considered that wearing the hemp modified EVA shoes for a long time can help to control or prevent the occurrence of fungal skin diseases.
4. Conclusions
Due to the unique structural characteristics of hemp stem powder, EVA foaming composites can significantly change the morphology and structure of the foam cells, reduce the density and hardness in performance, improve the resilience and compression deformation rate, so as to improve the portability and protection of the material. The inherent moisture absorption and quick drying property and antibacterial property of hemp stem powder also give the composite system with good moisture absorption and quick drying property and antibacterial property. When the content of hemp stem powder is 10-20%, the comprehensive performance of the composite material is the best, and the corresponding cell structure is more uniform, which can effectively meet the wearing needs of sports shoes, functional training shoes and leather shoes.

References
[1] Liu Y., Zheng Y.Y., Zhou J., Chen Z.J., Fan Z.M.. (2014) The Preparation and Characterization of EVA/Starch Composite Foaming Materials with Modified Antibacterial Powders. China Plastics Industry, 42: 16-20.
[2] Zhang Y.F., Zheng Y.Y., Liu Y., Xiao Y.Y.. (2014) The preliminary research on EVA sole foaming materials with wet grafted starch. Functional Materials, 15: 2253-2257.
[3] Fu M., Chen F.L., Cen L.. (2014) Research on modification and application of EVA. New Chemical Materials, 42: 220-223.
[4] Shi J. P., Chen G. H.. (2010) EVA/Hemp Core Flour Composite and Its Mechanical Property. Plastic, 39: 92-95.
[5] Hao X. M., Ma W.J., Gan G., Zhao P.C., Yang Y., Wang R.. (2013) Analysis of Novel Structure of EVA/Hemp Stem Powder Foam Materials. Advanced Materials Research, 627: 651-654.
[6] Yang Y., Hao X. M., Chen X. Y., Gao M. Z., Zhang G. J.. (2014) Study on Development of Hemp Stem-Based Panel. Advanced Materials Research, 887-888: 912-914.
[7] An L. X., Hao X.M., Wang J. M., Han L., Yang Y.. (2013) Study on Anti-bacterial Activity of Extractive Fractions of Hemp Stalk. Advanced Materials Research. 821-822: 1039-1042.
[8] Hao X. M., Chen X.. (2015) Study and Application on the Antibacterial Material of the Hemp Training Shoe. 2015 Forum on antimicrobial science and technology. Suzhou. 77-82.
[9] Hao X. M., Yang Y., An L. X., Wang J. M.. (2014) Study on the Extract and Application of Antibacterial Ingredient from Hemp Stem Powder. 2014 Forum on antimicrobial science and technology. Beijing. 103.
[10] Hao X. M., Yang Y., An L. X., Wang J. M., Han L.. (2014) Study on Antibacterial Mechanism of Hemp Fiber. Advanced Materials Research. 887-888: 610-613.
[11] Liu L., Chu H.J., Tu D.X., Hao X. M., Huang J.. (2018) Preparation and Properties of EVA/HSP composite foams. Journal of Shanghai University(Nature Science), 24: 782-790.
[12] Liu L., Tu D.X.. (2020) Effects of HSP content on microstructure and mechanical properties of EVA foamed materials. Journal of Shanghai University(Nature Science), 26: 208-215.