

Preparation of Foamed Composites from Poly (ethylene-co-Vinyl Acetate) and Aramid Fibers for Shoe Materials

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Abstract

Aramid fiber (AF), poly-m-phenylene isophthalamide, was used to reinforce foamed materials based on ethylene vinyl acetate copolymer (EVA) for shoe materials. In the first stage, the surface of the fiber was treated by different chemical reagent. The element content of AF surface was examined by means of energy dispersive spectrometer to record the effect of treatment on the surface. The morphologies of AF and the AF/EVA foams were investigated using scanning electron microscope. In a subsequent stage, the performance of those fibers as reinforcement in foamed composites of EVA was studied. The interface interaction between treated AF and EVA of the foamed samples were improved with adding AF treated either in alkali steam or in Friedel-Crafts reaction. Foamed composites with addition of AF displayed better physical properties, which showed a potential application value in shoemaking industry.

Keywords: Aramid fibre, ethylene vinyl acetate copolymer, interface, alkali steam, Friedel-Crafts reaction, foam

1 Introduction

Ethylene vinyl acetate copolymer (EVA), containing 12-30% VA, is a sort of thermoplastic elastomeric plastic used to produce independent porous foamed materials. It has been widely applied in fields such as sporting equipment, insulating material, and luggage liners^[1-3]. However, there are some disadvantages to EVA. For example, EVA foams with large expansion ratios are usually fraught with weaknesses such as severe material deformation, poor resistance to abrasion, proneness to slip, and low temperature hardening, which limit its further application in shoemaking industry^[4, 5].

It is well-known that the mechanical properties of the fibers reinforced polymer composites are influenced by the properties of the interface between the fiber and the resin matrix directly. Aramid fibers (AF) are a class of heat-resistant, strong, and high-modulus synthetic fibers. Because of their excellent mechanical and dynamic properties, such as high tensile strength, high tensile modulus, low density, good energy absorption, good resistance to

abrasion, good resistance to fatigue, and good dimensional stability, thus they are widely used as a good reinforcement material for polymer composites^[6-7]. Besides sporting goods, AF has been widely used in new fields of application, including but not limited to aerospace, electronics and appliances, civil engineering, bullet-proof devices, compressed natural gas tanks and diving respirators. However, the surface of AF is so chemically inert and smooth, which derives from the high crystalline of AF surface layer and the lack of the polar functional groups in the polymer molecule chain, that the adhesion between AF and the polymer matrix is very poor. How to achieve the combination between AF and polymer matrix has become a hot issue in research^[8-9].

From a perspective of improving the adhesion strength between the fibers and EVA matrix, active groups were introduced into the surface of the AF by surface modification to enhance its surface polarity, and by physical blending to form adhesion with the VA in the EVA molecular chain. Thus, AF/EVA composite foams with superior and wider properties were expected for value in shoemaking industry.

2 Material and Methods

2.1 Materials

EVA named 7350M containing 18% vinyl acetate was provided by Formosa Plastics, Taiwan. The density of the polymer is 0.938 g/cm³ and the melt flow index is 2.5 g/10min. AF, Yantai Tayho Advanced Materials Co., Ltd., Shandong, China. Stearic acid (SA) was supplied by Zhejiang Feixiang oil chemical Co., Ltd., Jiangsu, China. Azodicarbonamide (AC), used as a blowing agent (degradation temperature range was 202±3°C), was supplied by Jinlang Fine Chemical Co., Ltd. Fujian, China. Dicumyl peroxide (DCP), used as a crosslinking agent, was provided by Akzo Nobel Co., Ltd., Netherlands. Zinc oxide (ZnO), used as an activator, was supplied by Dongtai Hongyuan chemical factory, Jiangsu, China. Zinc stearate (ZnSt), used as a foaming coagent, was supplied by Dongguan Guohua chemical factory, Guangdong, China.

Preparation of the foamed samples

The internal system of the mixer was heated to the temperature of 100 °C. 300g EVA and the preprocessed AF was put into the mixer. AC, DCP, ZnO, ZnSt were then put into the mixer. The mixing procedure takes 10min. Upon completion of mixing, the AF/EVA composites were put in the two-roll mill, then sheared, tableted, cooled at room temperature and finally trimmed. The end material was cut into pieces and poured into the mold, which in turn, was put into the flat-panel curing press for mold foaming. The molding temperature is 180 °C. The molding time is 550s. The pressure is 10 mPa. Cooled and set, it was tested for properties and characterization.

2.2 AF Surface Modifications

(1) Oxidation treatment

AF was first degreased and then placed in a solution of 30% H₂O₂, with a temperature of 80 °C for 1h.

(2) Acid treatment

AF was first degreased and then placed in 30% H₂SO₄, H₃PO₄ or HNO₃ solution, for 1h.

(3) Alkali treatment

AF was first degreased and then placed in a 30% NaOH solution for 1h.

(4) Alkali steam treatment

AF was first degreased, placed in a 30% NaOH solution till soaked, wrapped in the polyester film, and then put in the solution at 120 °C. Timing begins when alkali vapor arose. It was processed for 30 minutes, and then washed until the pH value of the washing liquid turned 7.

(5) Friedel-Crafts reaction processing

Degreased AF and an excess of epoxy chloropropane were added to the three-necked flask, and then was heated using oil bath to 115 °C (the boiling point of epoxy chloropropane) for a period of time. AlCl₃ catalyst was added in three installments.

2.3 Characterizations

2.3.1 Scanning electron microscopy (SEM)-Energy Dispersive Spectrometer (EDS)

AF was gently stuck to a conductive tape, and then was coated with gold. The surface morphology of AF was scanned using a cold field emission Scanning Electron Microscopy (S4800, Hitachi, Japan), which is also an Energy Dispersive Spectrometer, for the purpose of elemental analysis. The working voltage is 5 kV.

2.3.2 Fourier transform-infrared spectroscopy (FT-IR)

After sufficient drying, AF samples were measured using Fourier Infrared Spectrometer (VECTOR-22, Brook, Germany) with attenuated total reflection (ATR) fixture so as to determine the change of surface functional groups.

2.3.3 Physical properties of the foamed samples

The density of the samples is using measured by using the electronics weight scale (HT-200, A&D, Japan).

The hardness (Shore C) of the surface of samples is measured with the Shore C hardness tester (Xihua, Guangdong, China).

A Desktop Tensile Strength Tester (AI-3000, Gotech, Taiwan) is used to obtain the tensile strength (stress), elongation-at-break (strain) and tear strength of the foamed sample at

room temperature. The tensile cross-head speed is 100 mm/min. The peel strength is measured by tearing the gap of a sample at a speed of 100 mm/min. All measurements are performed for three replicates and averaged to get the results.

3 Results and Discussion

3.1 AF Surface Modifications

3.1.1 SEM test for each type of AF surface modifications

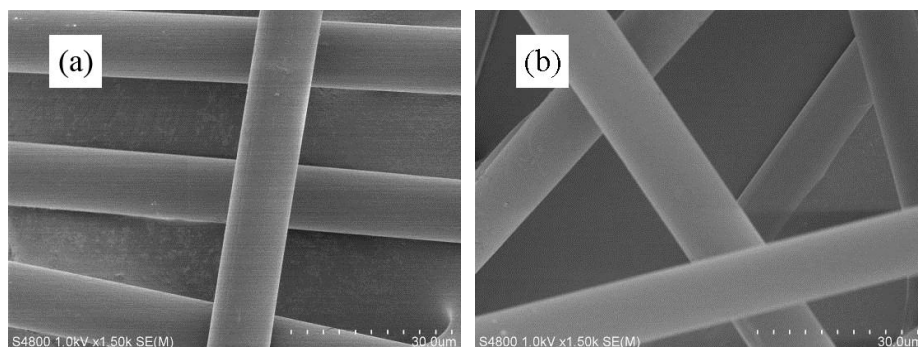


Fig.1 SEM images of AF modified by oxidation treatment, a) untreated AF, b) modified by H₂O₂.

Figure 1 was the SEM photograph of AF surface modification by oxidation treatment. The picture shows that the surface of untreated AF was smooth and complete, without breakage (Figure 1-a). After modified by H₂O₂, the surface of was Almost no change, which means the oxidation treatment of AF by H₂O₂ was ineffective. (Figure 1-b)

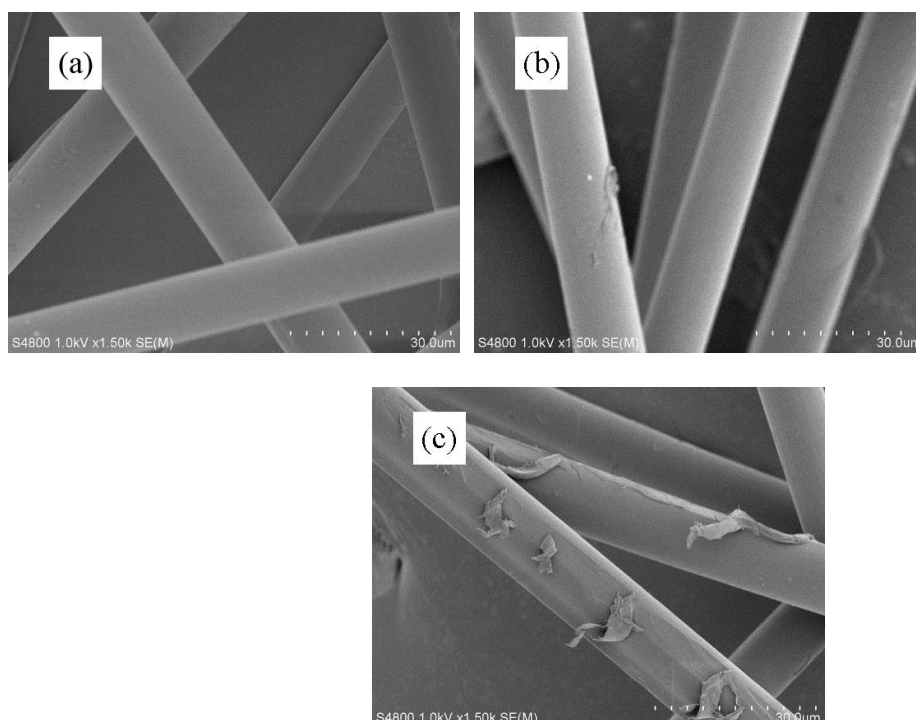


Fig.2 SEM images of AF modified by acid treatment, a) modified by H₂SO₄, b) modified by H₃PO₄, c) modified by HNO₃.

Figure 2 was the SEM photograph of AF surface modification by acid treatment. After H_3PO_4 and H_2SO_4 treatment, AF surface did not change significantly, only with few defects. AF surface flaked under HNO_3 treatment.

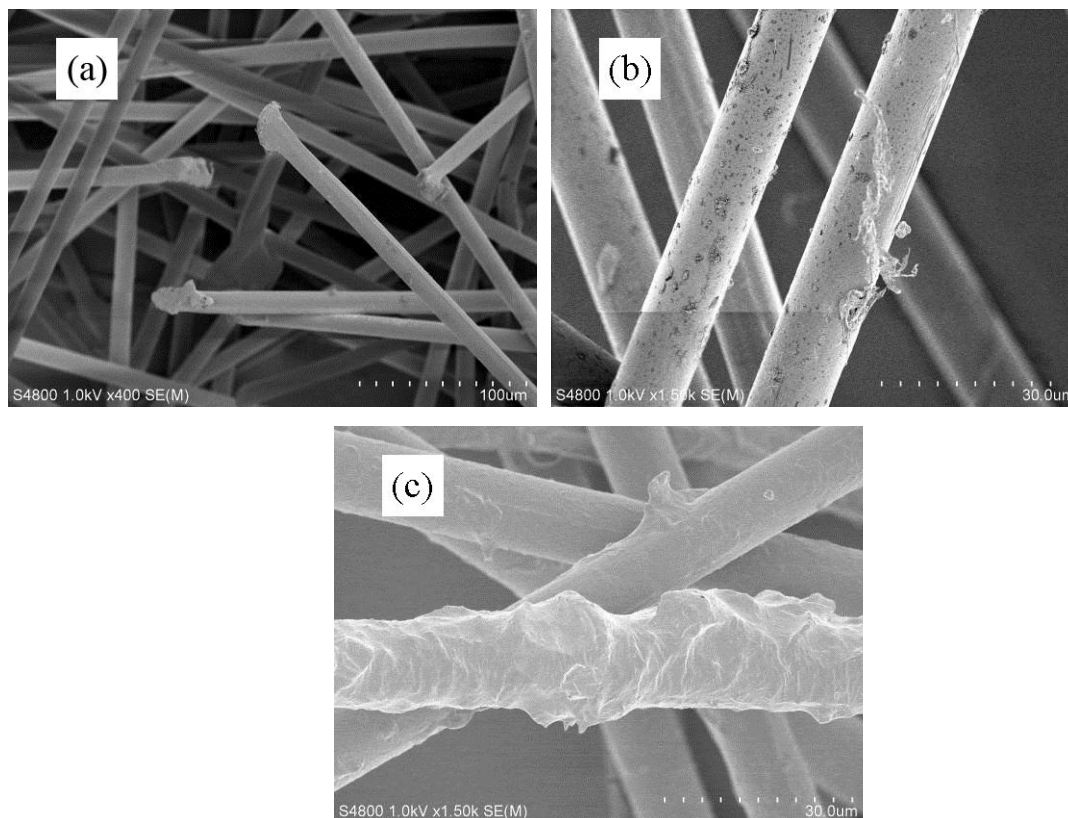


Fig.3 SEM images of AF modified by alkali treatment and Friedel-Craft reaction, a) modified by NaOH, b) modified by alkali steam, c) modified Friedel-Craft reaction.

Figure 3 was the SEM photograph of AF surface modification by alkali treatment. In the course of alkali treatment, when treated at 80 °C NaOH solution, AF displayed swelling at both ends (Figure 3-a). Fiber may be susceptible to alkaline hydrolysis at the ends. However, effect of the modification on the middle part is not obvious. When the temperature was raised to above 100 °C, using the same concentration of NaOH, alkali vapor (alkali steam method) arose, and there were obvious etching and wide flat grooves on the AF surface (Figure 3-b). Bulging and etching fragments, which are uneven and discontinuous in distribution, can be seen.

In contrast, AF surface became rougher after Friedel reaction processing (Figure 3-c). As can be seen in the figure, unlike the obvious concave caused by etching, there were tiny protrusions on the AF surface. Many big protrusions emerged on the fiber surface with uneven distribution. Visible shallow grooves, which look like small cracks could be seen. Epoxy chloropropane grafted onto the fiber surface.

The surface roughness of AF was significantly increased after being treated in alkali steam and Friedel-Craft reaction, which means, the surface area of the fibers was increased, which contributes to physical absorption force with the EVA matrix at later stage. The diffusion capacity of polymer matrix into the fiber was likewise improved.

3.1.2 EDS test for each type of AF surface modifications

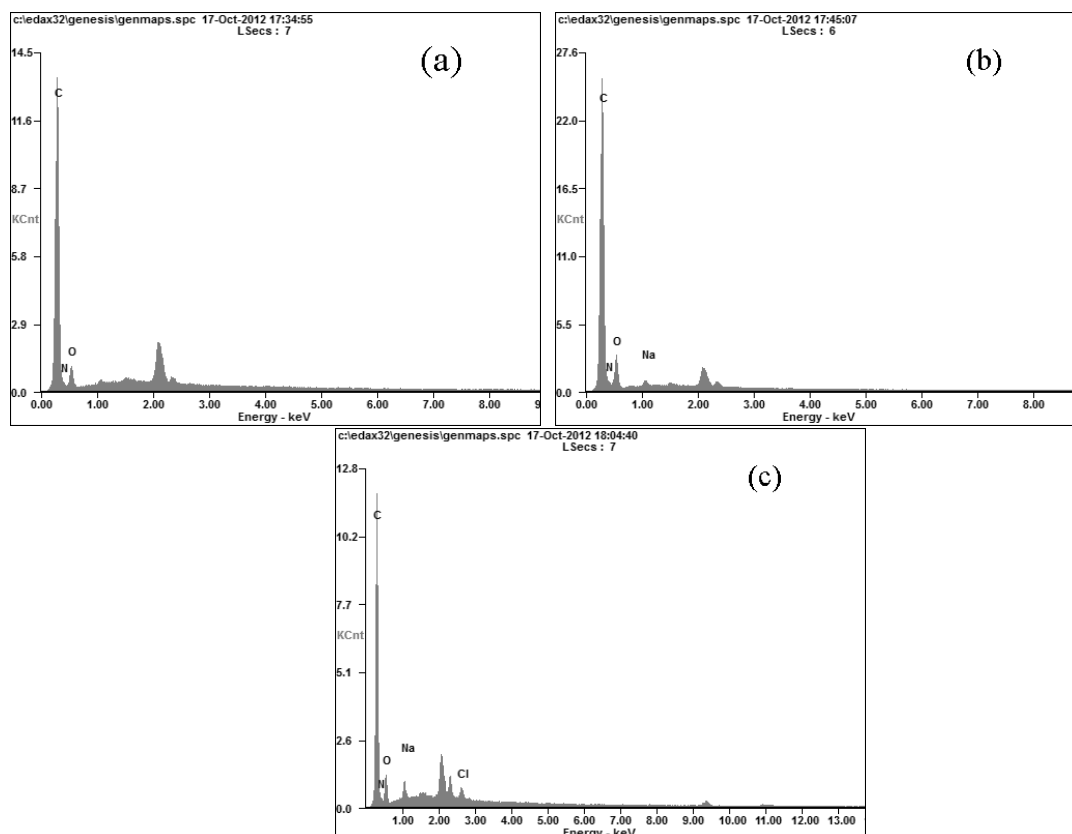


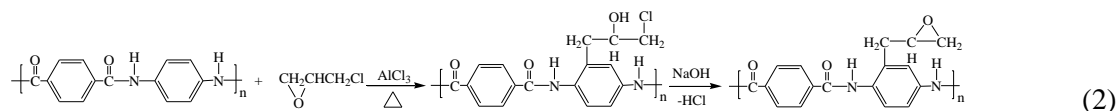
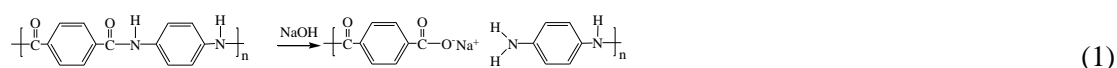
Fig.4 EDS images of AF modified by different approaches, a) untreated AF, b) modified by alkali steam, c) modified by Friedel-Craft reaction.

Element analysis was conducted on the original AF, AF treated in alkali solution and AF treated in Friedel-Crafts reaction. The EDS results were shown in Figure 4 and Table 1. It could be seen from Figure 4 that after the surface modification, changes occurred to the distribution of elements on the AF surface (energy was not analyzed here since the peak of energy in 2.1 refers to the coating gold). Table 1 showed the content of each element on the AF surface, which was calculated using computer software. As can be seen from Table 1, after alkali steam treatment, the content of O, N, and Na element increased by 3.19%, 1.02% and 0.65% respectively, while the content of C reduced by 4.86%. After the alkali steam treatment, the proportion of the element O in all elements was significantly increased, indicating that the hydrolysis reaction had occurred on AF surface.

Tab.1 elements content of AF surface modified by different approaches

elements	content		
	untreated AF	AF with alkali-decating	Af with Friedel-Craft reaction
C	73.88	69.02	74.15
N	11.91	12.93	9.53
O	14.21	17.4	13.91
Na	/	0.65	1.84
Cl	/	/	0.57

As can be seen from Formula 1^[10], theoretically, the hydrolysis of the amide bond on the AF surface would not increase the N content. However, due to hydrolysis reaction, the AF surface was etched and became rough. As a matter of fact, amino was exposed in the etched area, which results in the increase of N content measured by EDS. The proportion of Na in all the elements was smaller than the theoretical value. This might be attributed to the fact that some portion of -COONa had become -COOH after washing. The increase of the proportion of O, N and Na elements resulted in the decline of the proportion of C element.



As can be seen from formula 2^[11], Friedel-Crafts reaction process failed to break the chain segment. On the contrary, epoxy chloropropane grafted and wrapped around the surface of AF. The graft contained mostly C element, which resulted in the increase of C content. Due to the graft of epoxy chloropropane and the increase of Na, Cl, total element content was increased. As a result, the content of N and O decreased. However, there was much lesser decline in the content of O, which could be explained by the fact that there is one O in epoxy chloropropane. There was more increase in the proportion of O with respect to that of N before and after treatment of the Friedel-Crafts reaction, which proves that surface grafting reaction did occur. This is further confirmed by the increase of Cl element. The increase of Na showed that the AF surface might have been partially hydrolyzed at the late stage of the alkali treatment in the session of Friedel-Crafts reaction.

3.2 Properties of AF/EVA Composite Material

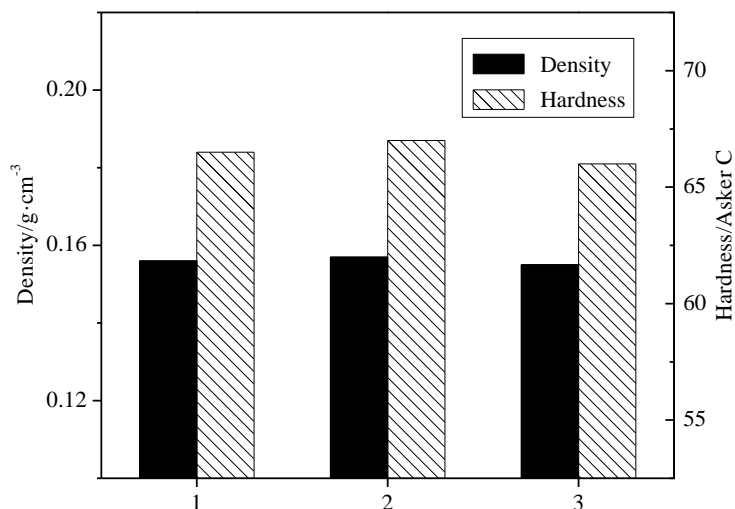


Fig.6 The effect on density and hardness of EVA foams 1) without AF, 2) with AF modified by alkali-decating, 3) with AF modified by Friedel-Craft reaction

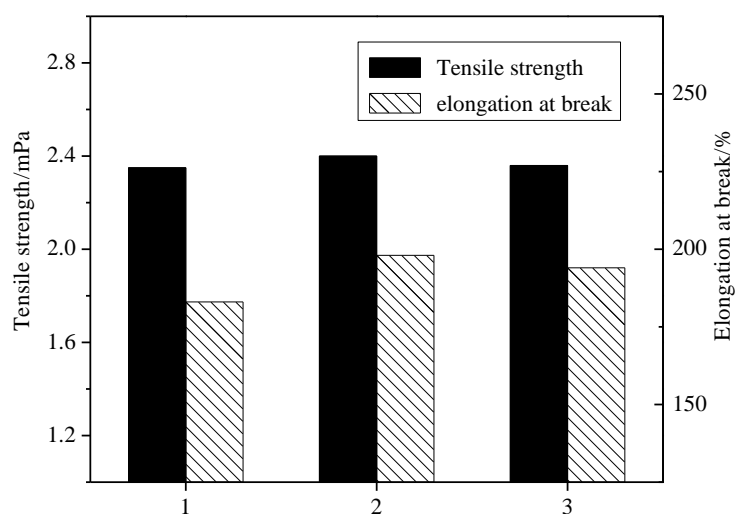


Fig.7 The effect on tensile strength and elongation at break of EVA foams 1) without AF, 2) with AF modified by alkali-decating, 3) with AF modified by Friedel-Craft reaction

The effect of AF treated by different modification methods on the density and hardness of EVA foam material was shown in Figure 6. The figure showed the two AFs which were modified using two different methods are not different in terms of density and hardness.

The effect of AF subject to different modification methods on the tensile strength and the elongation at break of EVA foam material was shown in Figure 7. The figure indicated that both the tensile strength and the elongation at break of the AF/EVA composite foamed material showed an upward tendency, after adding AFs subject to two different modification

methods respectively, which is valuable for shoe manufacturing.

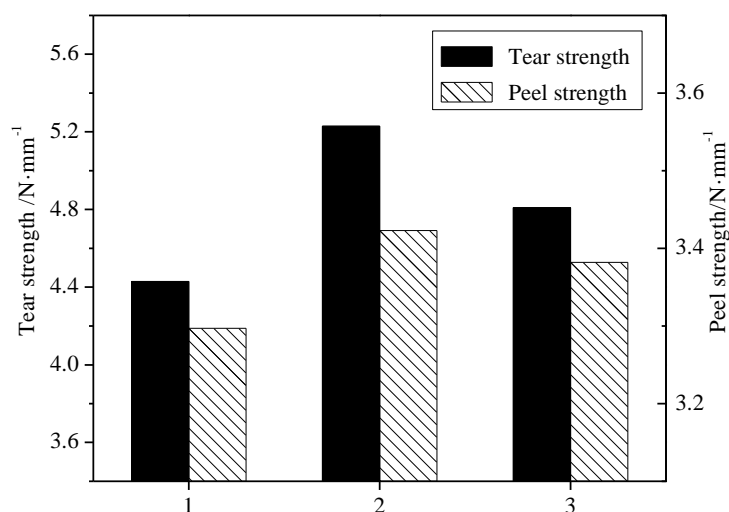


Fig.8 The effect on tear strength and peel strength of EVA foams 1) without AF, 2) with AF modified by alkali-decating, 3) with AF modified by Friedel-Craft reaction

The effect of AF subject to different modification methods on the tear strength and peel strength in EVA foam material was shown in Figure 8. The figure indicated that the tear strength and the peel strength of the AF/EVA composite foam material showed a rising tendency, after adding AF which underwent two different surface modifications. Such findings were consistent with the tendency of the tensile strength and elongation at break. There was a more significant increase in the tear strength and peel strength when adding AF treated in alkali steam than AF treated in Friedel-Crafts reaction.

After AF surface modification, either the alkali steam treatment or the Friedel-Crafts reaction, the polarity of the surface increases. Hydrogen bonds were formed with the polar vinyl acetate in the EVA molecular chain due to a certain increase in the adhesive force between AF and the EVA matrix. There was a more significant increase in the adhesive force when adding AF which underwent alkali steam treatment than AF which underwent Friedel-Crafts reaction. This may be attributed to the fact that there was more oxygen concentration on the surface, the polarity on the surface was high and as a result there was more adhesive force with EVA matrix. Hence, the mechanical properties of the composite foam material were largely enhanced.

4. Conclusion

Morphologic changes occurred to the surface of AF by alkali steam treatment and the Friedel-Crafts reaction. The two kinds of modification methods had successfully modified the surface of the AF and introduced oxygen-containing functional groups. AF treated either in alkali steam or in Friedel-Crafts reaction processing was added to the EVA foam material separately. As a result, there was a significant increase in the tensile strength, elongation at

break, tear strength and peel strength in the AF/EVA composite foam material, which was valuable for shoe manufacturing. AF surface polarity improved after surface modification, which resulted in its interfacial combination with the EVA matrix. The fiber served as a prop and the stress can be efficiently transmitted into the fiber when subject to the external force.

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6. References

- [1] Marc A. Jacobs, Maartje F. Kemmere, Jos T.F., Keurentjes., 2004 Foam processing of poly (ethylene-co-vinyl acetate) rubber using supercritical carbon dioxide, *Polymer*, 45(22), 7539-7547p.
- [2] Hilyard, N. C., Cunningham, A., 1995, *Low Density Cellular Plastics: Physical Basis of Behaviour*, Chapman and Hall, 36, 300p.
- [3] Jianzhong Ma, Fuquan Deng, Chaohua Xue, Zhouyang Duan., 2012, Effect of Modification of Montmorillonite on the Cellular Structure and Mechanical Properties of EVA/Clay Nanocomposite Foams, *Journal of Reinforced Plastics and Composites*, 31(17), 1170-1179p.
- [4]. Y.T. Sung, C.K. Kum, H.S. Lee., 2005, Effects of crystallinity and crosslinking on the thermal and rheological properties of ethylene vinyl acetate copolymer, *Polymer*, 46(25), 11844-11848p.
- [5]. I-Lung Chien, Tze Wei Kan, Bo-Shuo Chen., 2007, Dynamic simulation and operation of a high pressure ethylene-vinyl acetate (EVA) copolymerization autoclave reactor, *Computers & Chemical Engineering*, 31(3), 233-245p.
- [6] M. G. Dobb, D. J. Johnson, B. P. Saville., 1977, Supramolecular structure of a high-modulus polyaromatic fiber (Kevlar 49), *Journal of Polymer Science: Polymer Physics Edition*, 15(12), 2201-2211p.
- [7] M. Panar, P. Avakian, R. C. Blume, K. H, et al., 1983, Morphology of poly(p-phenylene terephthalamide) fibers, *Journal of Polymer Science: Polymer Physics Edition*, 21(10), 1955-1969p.
- [8] Tarantili P A, Andereopoiles A G, 1997, Mechanical properties of epoxies reinforced with chloridetreated aramid fibers, *Journal of Applied Polymer Science*, 65(2), 267-276p.
- [9] Taweechai Amornsakchai, et al., 1999, Composite of aramid fibre (poly-m-phenylene isophthalamide) thermoplastic elastomers (SEBS): enhancement of tensile properties by maleated-SEBS compatibiliser, *Polymer*, 40, 2993-2999p.
- [10] Taweechai Amornsakchai, Budsaporn Sinpatanapan, Sauvarop Bualek Limcharoen, et al., 1999, Composite of aramid fibre (poly-m-phenylene isophthalamide) thermoplastic elastomers (SEBS): enhancement of tensile properties by maleated SEBS compatibiliser, *Polymer*, 40, 2993-2999p.
- [11] Tie-Min Liu, Yuan-Suo Zheng, Jie Hu., 2010, Surface Modification of Aramid Fibers with New Chemical Method for Improving Interfacial Bonding Strength with Epoxy Resin, *Journal of Applied Polymer Science*, 118 (5), 2541-2552p.