EFFECT OF POST TREATMENTS ON THE SHRINKAGE RESISTANCE OF MELAMINE FOAM (MF)

Zhang Junxiong[1], Chen Zhaofeng[2], Shen Sheng[3] and Xue Songbai[4]

[1] MIIT Key Laboratory of Material preparation and protection technology Facing harsh environment and International Laboratory for Insulation and Energy Efficiency Materials, College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, P. R. China; zhangjunxiong126@163.com; sicl.msc.nuaa.edu.cn

[2] MIIT Key Laboratory of Material preparation and protection technology Facing harsh environment and International Laboratory for Insulation and Energy Efficiency Materials, College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, P. R. China; czf_msc@nuaa.edu.cn; sicl.msc.nuaa.edu.cn

[3] MIIT Key Laboratory of Material preparation and protection technology Facing harsh environment and International Laboratory for Insulation and Energy Efficiency Materials, College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, P. R. China; 953819515@qq.com; sicl.msc.nuaa.edu.cn;

[4] MIIT Key Laboratory of Material preparation and protection technology Facing harsh environment and International Laboratory for Insulation and Energy Efficiency Materials, College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, P. R. China; xuesb@nuaa.edu.cn; msc.nuaa.edu.cn

ABSTRACT

The thermal treatment and resin modification were employed to improve the thermal shrinkage resistance of the melamine foam in this paper. The result indicated that both of this two methods could improve the thermal shrinkage resistance of MF. The minimum contraction percentage were 0.07% and 0.5%, when the conditions were the thermal treatment at 200°C for 40 h and 3% phenolic formaldehyde resin(PF) treatment at 150°C for 0.5 h, respectively. The result of FTIR spectrum proved the mechanisms that the reaction of free functional group in MF, $–NH_2$ and $–CH_2OH$, formed a novel cross-linking of $–NH–CH_2–$, which increased the degree of crosslinking of the MF and improved its shrinkage resistance on heat. However, the effect of the PF on MF was covering a layer of stable PF to enhance the strength of the foam structure and reduce the thermal shrinkage resistance, and its effect was a little inferior.

Key word: Melamine foam (MF), thermal treatment, thermal shrinkage resistance, FTIR

1 INTRODUCTION

Melamine foam is a kind of original polymer foam materials with special 3D network that 99% of its bulk is porous filled with air[1]. Therefore, its effect on thermal insulation is excellent as well as its acoustic absorption[2]. Meanwhile, the inflame resistance of MF is much better than others for its 67% percentage nitrogen content in the molecule, whose LOI (Limited Oxygen Index) is 40 and matches the UL94-V0 standard for the flame-resistant materials[3]. For owning various aspects of outstanding performance, MF is widely used for thermal insulation and acoustic absorption in vehicles, trains, building and other fields[4].

However, there are some defects limited the application and development of MF, such as the perfect compatibility with water and oil[5], high degree of volatile components, instability under the conditions of heating, acid or alkali treating. Therefore, it's necessary to improve its property.

Yang[3] improved the fire retardancy and anti-shrinkage of MF by covering multi-layers of nano–Coatings of ammonium polyphosphate(APP) and chitosan(CH) on it. And, it showed that the LOI of MF raised to 47 with two-bilayer CH-APP covered on the structure of MF, which also improved the anti-shrinkage of MF. Wang[6] mentioned the utilization of polyving akohol(PVA) would enhance the mechanical properties of MF as well as decrease its pulverization. Li[7] showed that the addition of 1,4-butanediol would enhance tear-resistance as well as decrease its fragility, and the optimum content of the 1,4-butanediol was 10wt.%, when its compressive strength was 0.947MPa, its pulverulent ratio was 2.9%, its LOI was 36.7. Zhang[8] involved that the improvement of the properties of MF could be realized by the change of its process of foam moulding, whose optimum technological parameter was that its viscosity was 1500 mPa·s, and its heating condition was 1min with microwave. Yang[9] employed the PEG-200, caprolactam, diethylene glycol and glycol to modify MF and foamed it at 80°C. It showed that the MF obtained the optimum properties under the conditions of 14wt.% caprolactam, 1547.5 mPa·s viscosity and foaming at 90°C as well as PH keeping in 9.

According to above investigation, it was obvious that the properties of MF could be enhanced by modifying with either different reagents or foaming process. However, there existed inadequacy, such as its operability and complexity of process, the environmental issue, et al. And, the pre-treatment of the thermal treatment and resin modification were employed to improve the thermal shrinkage resistance of the MF in this paper. The FTIR spectrum was used to test the changes of the functional groups to verify the reaction mechanisms. The SEM was also utilized to evaluate the coating PF on the framework of the MF.

2 EXPERIMENTS

2.1. Materials and Equipment

MF with a density of 7 kg/m^3 and without flame retardant additives, was purchased from Henan Zhongyuan Chemical Group Co., Ltd, and it is flexible foam with open cell. Phenolic resin (PF, 2123-4) was purchased from Xinxiang bouma sail industrial Co., Ltd. Ethyl alcohol (AR, 99%) was purchased from Nanjing Chemical Reagent Co., Ltd. All materials were used as received without further purification.

The circulation oven (DHG-9036A) was from Shanghai Jinghong Scientific Instrument Co., Ltd. The FTIR spectrum (Thermo Electron Nexus 670) was from America Thermal Fisher Scientific Co., Ltd. The Scanning Electronic Microscope (SEM, Phenom XL) was from Phenom Scientific Instrument (China) Co., Ltd. The Vernier calliper was from Shanghai Measuring Tool Co., Ltd.

2.2 Layer deposition

The PF deposition solution was prepared by dissolving the PF 2123-4 with Ethyl alcohol. This aqueous solution was magnetically stirred for 1 h until the PF was completely dissolved. The concentration was 0.5~5wt.%, the resulting solutions were used without any adjustment. Fig 1 shows the schematic representation of preparing process of PF layer-by-layer (LbL) assemblies.

The assembly of PF is based on Van der Waals' force as driving force, and it is easy for PF adsorbing on the surface of melamine foam as the first layer due to hydrogen bonding force. The substrate was dipped into the PF solutions, pressed and dried to be one bilayer. The substrate was first immersed into the PF solution for 5 min and pressed to decrease its residual solution twice and then dried at 150℃, 180℃ and 200℃, respectively. The process was repeated until the required number of bilayers was built for each system. After achieving the desired number of bilayers. To characterize the PF coatings, 1%, 3% and 5% PF solution were prepared for deposition.

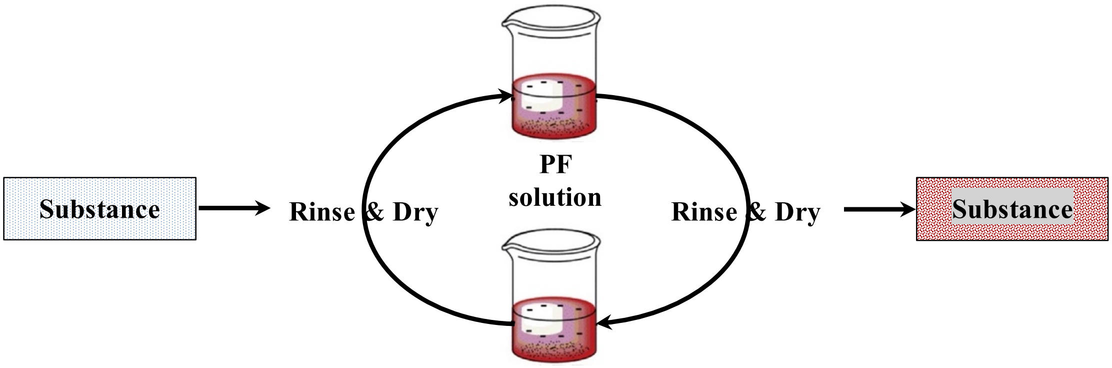

Fig 1. Schematic representation of layer-by-layer (LbL) assembly with PF solution. This process was repeated until the desired number of bilayers were deposited.

2.3. Measurements and characterization

Fourier transform infrared spectroscopy (FTIR) was performed on a Thermo Electron Nexus 670 spectrometer with the ATR of Spectra-Tech Foundation Endurance using 32 scans in the frequency region of 4000~400 cm^{-1} at a 4 cm^{-1} resolution. The morphologies of the uncoated and coated MFs were observed using scanning electron microscopy (Phenom XL). A thin layer of gold was sprayed on the surface prior to SEM observation. The dimension of all samples was 30*30*20 mm^3. The shrinkage of the MF samples was according to the China National Standard GBT 8811-2008[10].

3 RESULTS AND DISCUSSION

3.1. Effect of thermal treatment and PF coating on MF

It is obvious that the viscosity of MF resin was controlled during foaming process, which means the reaction between formaldehyde and melamine is incomplete, and varies of active radical groups, $–CH_2OH$, $–NH_2$ and $–N–CH_2$- exist in the MF[11]. It indicates that the MF is reactive under proper circumstances. It was reported[9] that the crossing reaction between formaldehyde and melamine is the dehydration reaction between$–CH_2OH$ and $–NH_2$ or –NH–, and reaction occurring while heating or acid-catalysis, and it could react with other substance with appropriate functional group as well. Therefore, thermal treatment and PF coating were employed to improve the shrinkage resistance of MF.

Fig 2 showed the relationship between the shrinkage percentage of time under the thermal treatment circumstance (Holding at 200℃). It indicated that the shrinkage percentage of MF decreased with the holding time increasing, however, the MF did not shrink accompanied by the heating time elongating. While holding at 200℃ for 70h or longer, the size of MF sample did not change either. Therefore, 70h at 200℃ is optimum parameter for thermal treatment of MF. But, it's needless for the engineering application because of the waste of time and energy for thermal treatment of MF, and 0.5% shrinkage percentage is acceptable as well as its resource waste.

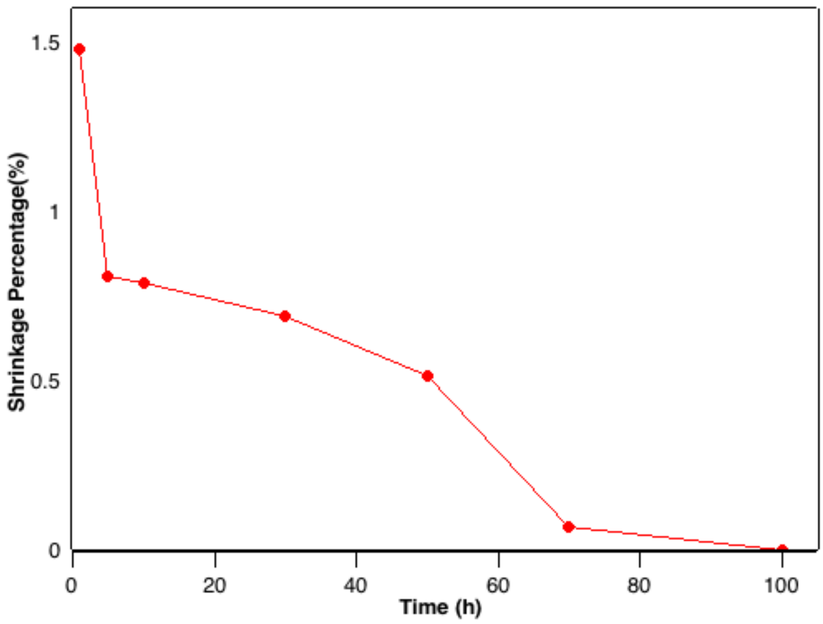

Fig 2. Relationship of time and Shrinkage percentage while thermal treating

Fig 3 showed the comparison of the effects of thermal treatment and PF modification on the shrinkage resistance of MF. It was obvious that the shrinkage resistance of MF with thermal treatment or PF modification was improved, and the shrinkage percentage of MF was 1.5% without any treatment. While holding at 200℃, 0.8% shrinkage occurred for 2h without coating and 0.05% for 40h. For PF coating, the results were 0.5% shrinkage with 3% PF coated accompanied by 0.5h heating at 200℃, and 0.8% with 5% PF coated accompanied by 0.5h heating at 200℃. And, it was obvious that both of this two ways shown their excellent effects on improve the shrinkage resistance of MF as well as great performance. Therefore, the ATR-FITR was utilized to study the reaction mechanism occurred during the treatment, and the results was listed in Fig 3 and 4.

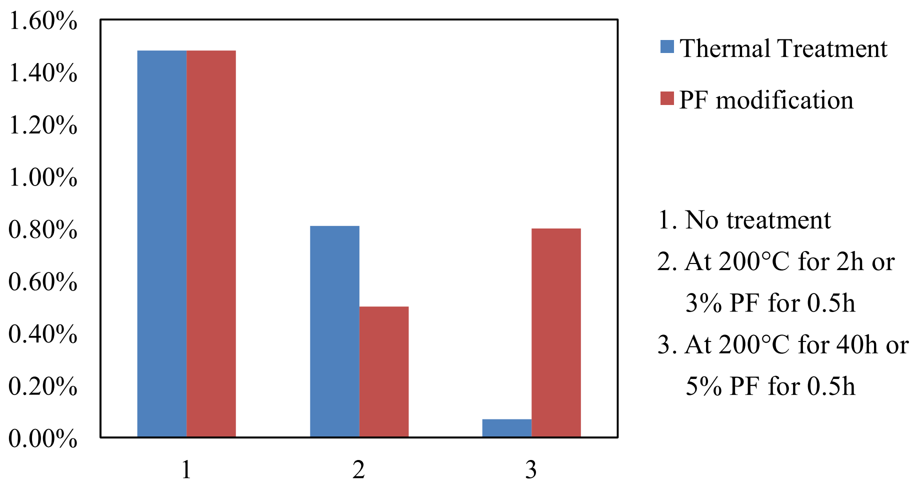

Fig 3. Shrinkage resistance of MF with different treatments

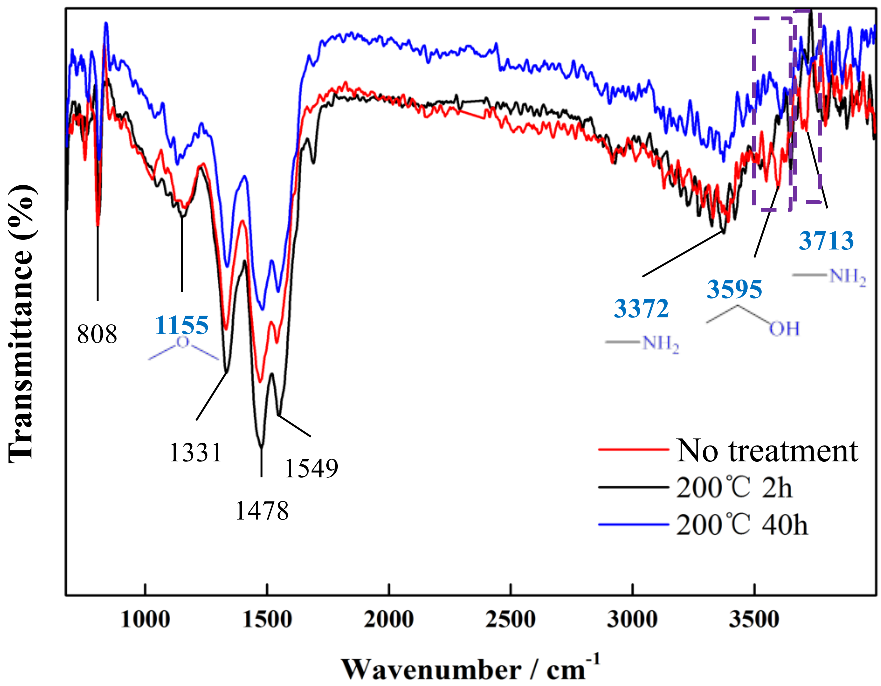

Fig 4. FRIT spectra of MF with/without thermal treatment

The spectra of ATR-FTIR shown in Fig 4 was the spectra of MF with different thermal treatment processes. For the spectrum, the absorption at 1331, 1478 and 1549 cm^{-1} were the characteristic peaks of the thiotriazinone group in MF. The absorptions at 3372 and 3713 cm^{-1} are attributed to $–NH_2$. The absorptions at 3595 $cm^{-1}$are attributed to the –OH. And, it's obvious that the peak at 3595 cm^{-1} disappeared from the curves with thermal treatment. Meanwhile, the peak at 3713 cm^{-1} for free $–NH_2$ disappeared either with the peak of –OH at 3595 cm^{-1}. The disappearance of –OH and $–NH_2$ proved their reaction for forming the $–NH–CH_2–$.

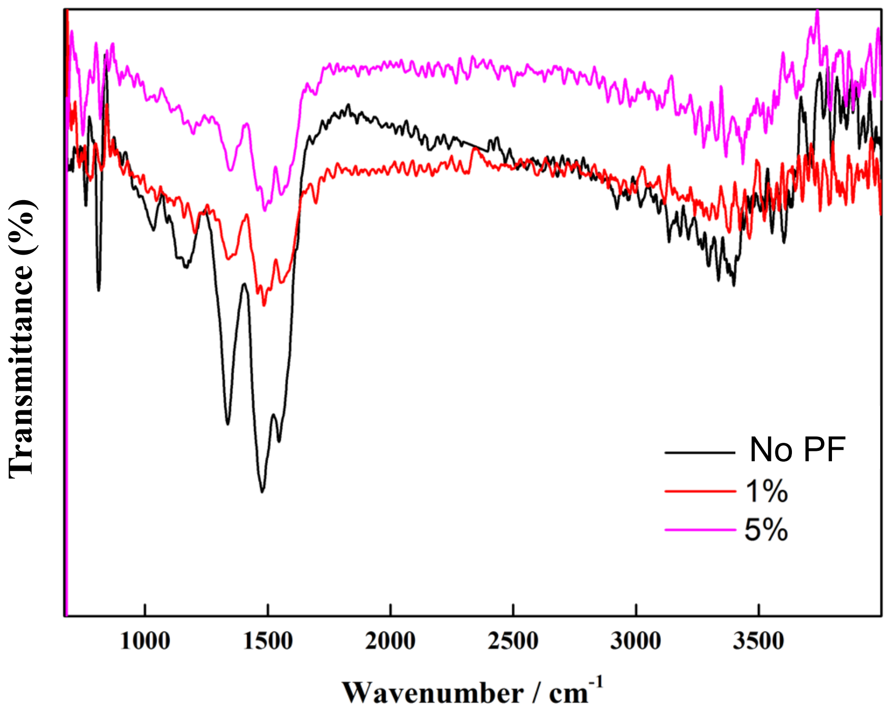

Fig 5. FRIT spectra of MF with/without PF modification

The spectra of ATR-FTIR shown in Fig 5 was the spectra of MF with different concentration of PF modified. It was obvious that the three curves were almost the same, but the peak intensity of MF without PF modification was much higher than others, which meant the PF coating covered on MF foam partially. And, the SEM photograph confirmed it.

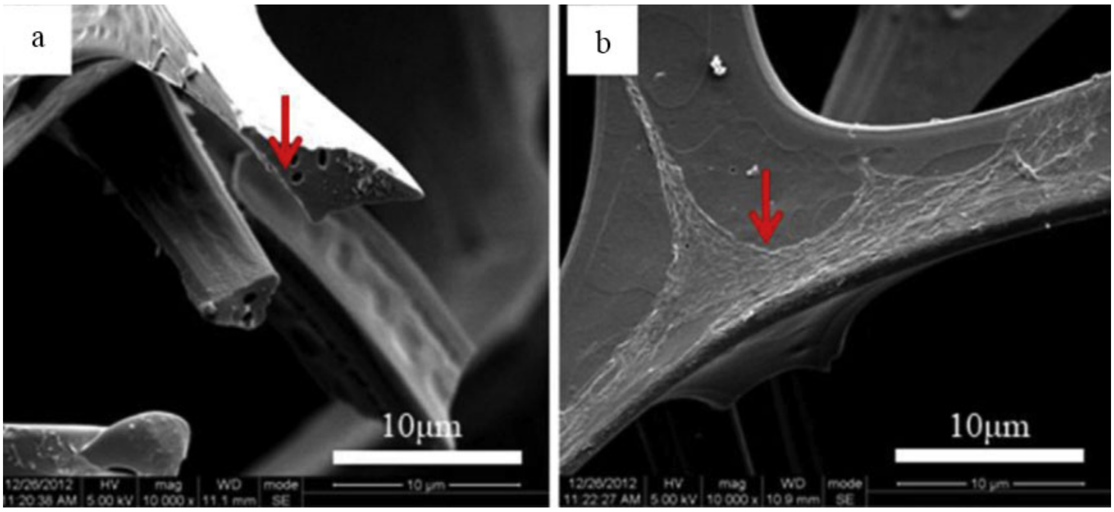

Fig 6. SEM of PF coating on MF

4 CONCLUSION

In this paper, it has been demonstrated that the thermal shrinkage resistance of the melamine foam is enhanced by either the thermal treatment or PF resin modification. The result indicated that the minimum contraction percentage were 0.07% and 0.5%, when the conditions were the thermal treatment at 200°C for 40h and 3% PF resin treatment at 150°C for 0.5 h, respectively. The FTIR spectrum proved the mechanism occurred in MF was the formation that the novel crosslinking, $-NH-CH_2-$, by the reaction between $-NH_2$ and $-CH_2OH$, which increase the degree of crosslinking MF to improve its shrinkage resistance on heat. However, the effect of the PF on MF was covering a layer of stable PF to enhance the strength of the foam structure to improve its thermal shrinkage resistance.

ACKNOWLEDGEMENTS

This paper is supported by the funded of the International Technology Cooperation and Exchanges, No.2015DFI53000.

This paper is also supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions(PAPD).

REFORENCE

[1]. Gonzales D A, Bogaerts I, Childs S L, et al. Process for producing a heat-compressed melamine foam cleaning implement[P]. US20090197072, 2009.

[2]. Jaouen L, Renault A, Deverge M. Elastic and damping characterizations of acoustical porous materials: Available experimental methods and applications to a melamine foam[J]. Applied Acoustics, 2008, 69(12):1129-1140.

[3]. Yang J C, Cao Z J, Wang Y Z, et al. Ammonium polyphosphate-based nanocoating for melamine foam towards high flame retardancy and anti-shrinkage in fire[J]. Polymer, 2015, 66:86-93.
[4]. Geebelen N, Boeckx L, Vermeir G, et al. Measurement of the Rigidity Coefficients of a Melamine Foam[J]. Acta Acustica United with Acustica, 2007, 93(5):783-788.
[5]. Xu Z, Miyazaki K, Hori T. Dopamine‐Induced Superhydrophobic Melamine Foam for Oil/Water Separation[J]. Advanced Materials Interfaces, 2015, 2(15).
[6]. Wang Weidong, Zhang Wiaoxian, Luo Song, et al. The preparation and properties of modified melamine foams[J]. Functional material, 2012, 43(24):3381-3385.
[7]. Li Huaqiang, Sun Jie, Qian Kun, Wei Qingqing, et al. Study on Modified Rigid Melamine Foam with 1,4-butanediol[J]. Application of engineering plastics, 2015, 43(8):6-11.
[8]. Zhang Xueli, Wang Kejian, Jiang Honggang, et al. Process optimization of preparing melamine formaldehyde foam[J]. Journal of Chemical Engineering, 2015, 66(s1):343-348.
[9]. Yang Fan, He Yun, Han Xianchao, et al. Preparing Technology and Formulations Optimization for Foaming Modified Melamine Formaldehyde Resin[J]. Application of engineering plastics, 2015, 43(5):13-17.
[10]. GBT 8811-2008, Rigid cellular plastic—Test method for dimensional stability[S].
[11]. Sun Zhongfei. Research on the technology of modified melamine formaldehyde/ phosphate composite foamed thermal insulation material[D]. Harbin Institute of Technology, 2012.