The mechanical and thermal characteristics of phenolic foam reinforced with kaolin powder and glass fiber fabric

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Abstract. In this work, kaolin powder and glass fiber fabric were added to PF in order to improve its thermal stability and mechanical property. Micro-structures of carbonized PF with kaolin powder were inspected by scanning electron microscopy (SEM) to demonstrate the filler’s pinning effect. SEM results illustrated modified PF had well morphology after high-temperature heat treatment. The Fourier transform infrared spectrometer (FTIR) test was carried out and found that kaolin powder only physically dispersed in PF. The compression test and thermal weight loss test were done on two groups of modified PF (Group A: add powder and fabric; Group B: add powder only). Results showed that all modified PF were better than pure PF, while foams with powder and fabric showed better mechanical characteristic and thermal stability compared with foams with powder only.

1. Introduction

Recently, rigid polymer foams (polyurethane, polyvinyl chloride, polystyrene and etc.) have attracted lots of attention [1]. Due to their porous structure and high compressive modulus, they can insulate sound and heat while resisting shock, which have been applied as functional materials on buildings, shipping and aerospace [2-3]. Of special note is that there are two types of pass inside foams, open pass and closed pass[4].The latter kind of foams have better thermal and sound insulation, as well as good impact resistance than former foams. In real cases, it is common that both open pass and closed pass exist in polymer foams, and properties of foams can be changed by alternating the proportion of two kinds of pass.

Among all rigid polymer foams, phenolic foam (PF) stands out because it can be fabricated by simple procedures and available ingredients, which render PF to be relative cheap [5]. Besides, unlike polyurethane or polystyrene foam, PF can maintain perfect thermal stability from -196°C to 200°C and has a high self-ignition point of 400°C. Plus, it releases limited toxic gas and produces no dropping during combustion, which makes it more suitable to use as fireproof wall materials than other rigid polymer foams. However, PF is restricted in use owing to some mechanical defects. During free foaming, PF will produce various sizes of pores thus uneven density, which is detrimental for its physical performances-i.e. causing it to be brittle and fragile.

Many studies have been done in order to improve mechanical properties of foams [6]. Some researchers induce active chains to hard segments of phenolic resin through chekaolinl reaction. Yang et al. [7] added polyurethane prepolymer to PF in order to improve its mechanical and thermal
retardant properties. Smith [8] used polyisocyanate to strengthen the mechanical property of PF. But most of these chekaoi linl agents are quite flammable, lowering the thermal characteristic of the PF. Additionally, complex procedures have to be adopted during in-situ polymerization, which will make materials expensive and difficult to mass produce. Thus other researchers have turned to physical fillers to solve the pr2 oblem. Zhang et al.[9]and Chen et al. [10]added muti-wall carbon nanotube to the PF and found improvement of its physical characteristic. Desai et al. [11] strengthened the property of the foam by inducing glass and aramid fiber to it. However, merely adding zero-dimensional or uni-dimensional fillers into the PF cannot hold the matrix together, which will result in high pulverization ratio. So in this work, two-dimensional glass fiber fabric as well as kaolin powder is added to the PF in order to greatly increase its mechanical behaviors.

Kaolin [12-14] powder is chosen to be filler due to benign adhesion and high surface energy thus can be easily attached to backbones of PF, helping to increase the mechanical property of PF before and after high-temperature heat treatment. In addition, kaolin powder can increase flame retardation since it is composed of SiO$_2$ and Al$_2$O$_3$. While we can better take advantage of PF with kaolin powder when it is exposed under a higher temperature, under which the powder tend to sinter and form a hard solid, thus stabilizing PF and preventing fire from spreading. At the meantime, this filler is relatively cheap compared with other additives, so it is quite possible to put our production into widespread use in the future.

The glass fiber fabric is adopted in order to increase the toughness of the PF [15]. What is more important, PF with only kaolin powder is inclined to collapse when fire first start (the temperature is not high enough), but if glass fiber fabric is added to the PF, relatively fixed shapes can be maintained at wide temperature range.

In this work, two groups of the PF (A and B) were fabricated. Group A were foams with 15 layers of glass fiber fabric and kaolin powder while group B contained only the powder. For each group, a series of gradient experiments were designed with different proportion of kaolin powder. Then their mechanical performances were tested by compression test, and their thermal stability was analyzed in detail, leading us to find the perfect proportion of the filler. The infrared spectroscopy was carried out to test whether glass fiber fabric and kaolin powder reacted with the resin or not. Micro-structures of PF were tested specifically to explain their unique behaviors. The modified PF was found having excellent toughness and thermal stability.

2. Experimental session

2.1. Materials
Resole-type phenolic resin (solid content75%-79%, viscosity2000~3000mPa·s) was supplied by Jining Huakai Resin Co., Ltd., Shandong, China. Tween 80(surfactant), P-toluene sulfonic acid (curing agent) and n-pentane (foaming agent, b.p.36.1°C) were supplied by Sinopharm Chekaoi linl Reagent Co., Ltd. Kaolin powder was obtained from Haihua Flame-Retardant Materials Co., Ltd., Qingdao, China. The glass fiber fabric was supplied by Sinamascience & Technology Co., Ltd..

2.2. Preparation procedures for the phenolic foams
The procedures for fabricating foams in group A were:
(1) Adding Tween 80(8wt% with respect to resin) and kaolin powder(0,10,20,30,40,50 wt%) to phenolic resin(18g) in a flask, then stirring the mixture at 500rpm for 8min under 25°C using impeller.
(2) Pouring the mixture in a beaker, then rapidly mixing n-pentane (10wt%) and P-toluene sulfonic acid (10wt%) to the mixture, then stirring them at 500rpm for 3min under 20°C. Low temperature and swift actions were needed in case the mixture started foaming and curing inappropriately.
(3) 15 layers of glass fiber fabric were firstly cut out in shape (100mm × 100mm).Pouring some mixture in a mold (length (l) × width (w) × thickness (t) = 100mm × 100mm × 15mm) and using a brush to apply the mixture evenly. Then put a piece of fabric on it. Repeating this step till all the fabric
and the mixture were added in the mold. Each specimen maintained weights of phenolic resin to be the same.

(4) Putting the mold into vulcanizing machine, which was set at 85°C. After 5min of free foaming, pressure was added to the mold after gases have been all squeezed out and the mixture was kept at 85°C for 30min. Then foams were obtained.

(5) Putting the foam into a drying oven under 70° C for 1.5h, in order to get rid of remaining water and help foams to cure thoroughly. Then samples of foams with glass fabric and powder (G/K-PF) were cut carefully for future tests.

The preparation of foams in group B followed same steps as above except adding fabric to the mold. The samples of foams (K-PF) were then cut delicately.

2.3. Characterizations

Micro-structures, such as morphology of pores and backbones before and after high-temperature heat treatment, were tested specifically using ULTRA PLUS43-13 scanning electron microscopy (SEM). In SEM test, foams were cut into specimens (5mm × 5mm × 3mm) and observed under zoom magnification of 200, 500. The average diameter of pores \( \bar{d} \) was calculated using the formula:

\[
\bar{d} = \frac{\sum N_i d_i}{\sum N_i}
\]  

(1)

In this formula, \( L \) was the measuring scale; \( N_i \) was the \( i \)th pore; \( d_i \) was the diameter of the \( i \)th pore.

The FTIR test was carried out on samples A/0wt% and A/10wt% by Nicolet Nexus 470 Fourier transform infrared spectrometer. The samples were ground and mixed with KBr, then were prepared as tablets to test.

The apparent density \( \rho_f \) (kg/m\(^3\)) was measured according to GB/T6434-2009 under 25°C. Both specimen before and after high-temperature heat treatment were tested.

Then compression tests were done by universal testing machine (mode RGM-4XXX) according to GJB1585A-2004 at room temperature, in order to figure out the compressive strength (MPa) of each specimen. The displacement speed of the machine was adjusted to 1mm/min until the yield point existed, or until the compression deformation was more than 10% if there was no yield point. To avoid the influence of foam densities in each group, specific compressive strength (MPa·g\(^{-1}\)·cm\(^3\)) was also calculated using the formula:

\[
\sigma_s = \frac{\sigma_m}{\rho_f \times 9.8}
\]  

(2)

In the formula, \( \sigma_s \) was the specific compressive strength; \( \sigma_m \) was the compressive strength; \( \rho_f \) was the density of the foam.

Thermal stability was tested by measuring weights of samples before and after putting into Muffle furnace. Our samples were kept in the furnace for 5min under 600°C. Each sample was tested in triplicate to provide relative accurate results.

3. Results and discussion

3.1. Analysis of SEM

In the Fig.1, the micro-structure of K-PF foams before and after high-temperature heat treatment were investigated. Fig.1 (a) showed pores of pure PF. According to the test, PF bore closed pass, which meant they had high thermal stability. However, its cells were big and uneven (\( d =192\mu m \)), rendering
thin pore membranes and weak backbones, which could illustrate its poor mechanical property. Fig.1 (b) and (c) showed the micro-structure of K-PF/10wt% (means PF in group B, which has 10% of the powder). It can be seen that cells were smaller (d = 92µm) and more uniform after adding kaolin powder. Of special note was that the powder was dispersed mainly in backbones, which acted like the nail in walls, thus it could help the foam to resist stress and maintain its morphology (Pinning effect). Fig.1 (d) and Fig.1 (e) showed the morphology of K-PF/10wt% after high-temperature heat treatment. After being put in Muffle furnace for 5min, pore membranes disappeared and only backbones of the foam remained. Further investigating Fig. (e), some little pores formed on backbones, which was mainly because of the volatilization of low-molecular compounds and incomplete decomposition of the resin. However, backbones could remain its morphology and had mechanical strength with the help of our refractory inorganic filler.

Fig 1. SEM analysis of PF (a) before high-temperature thermal treatment, pure PF;

3.2. Analysis of infra-red spectrum (FTIR)
Fig.2 showed spectrograms of pure PF and G/K-PF/10wt%. During curing process, reactions mainly happened among benzyl alcohol, phenolic hydroxyl and active hydrogen on the phenol ring. From the spectrogram, 3494cm⁻¹, 3024cm⁻¹, 1302cm⁻¹ and 1135cm⁻¹ were vibration absorption peaks of Ph−OH, methylene, Ph-O of phenolic hydroxyl and ether bond. Absorption peaks of 1579cm⁻¹ and 1484cm⁻¹
indicated vinyl on the benzene ring. And absorption peak of 786 cm$^{-1}$ meant ortho-substituted groups on the benzene ring. Comparing two curves, peak positions and shape of peaks remained the same after adding fillers to PF, which indicated both glass fiber fabric and kaolin powder did not react with the matrix.

Fig 2. FTIR spectrograms of PF and G/K-PF/10wt%.

3.3. Analysis of density

Densities for all specimens were shown in Fig. 3. Since kaolin powder would not react with the resin matrix or decompose during processing procedures, it could be seen that with the increasing amount of the filler (the weight of mixture increased), densities of foams in both groups grew. When further investigating these graphs, difference of slopes was noticed. In group B (K-PF), slopes decreased when more amount of filler added to it. That was because particles with high proportion tended to aggregate, which acted as nucleating agent and led to formation of large pores around it. Thus PF with high percentage of filler were more likely to contain many large cavities and had relatively small densities. However, slopes in group A (G/K-PF) increased dramatically. Since there were both fabric and filler when forming foams, it would become increasingly harder for gas to form pores and escape from the matrix. So for G/K-PF/50wt%, which contained a great many uneven pores and rough surfaces, bearing poor mechanical properties.

In Fig. 4, densities of PF after high-temperature heat treatment were also investigated. Since the temperature for a normal fire was 400°C, a temperature higher than that (600°C) was set to find out thermal stability of specimens. At this temperature, not only additives, like surfactant (Tween-80) would degrade, but chains of PF would break and release many low molecular compounds (carbon monoxide, carbon dioxide, methane, cresol, xylenol and etc.). When the temperature was higher than 600°C, the benzene ring would start open-loop decomposition and the whole matrix would carbonize. From Fig. 4, density of K-PF/0wt% decreased 45%, while density of G/K-PF/0wt% decreased 34%. It clearly showed that the glass fiber fabric could prohibit the release of a large amount of gas, obstruct movement of main chains, thus helping the whole foam remain its shape during the fire. These results showed that by adding kaolin powder and glass fiber fabrics to PF, it exhibited higher thermal stability than pure PF.
Fig 3. Densities of PF before high-temperature heat treatment (a) G/K-PF foams; (b) K-PF foams.

Fig 4. Densities of PF after high-temperature heat treatment (a) G/K-PF foams; (b) K-PF foams.

3.4. Analysis of Mechanical Performance

The compressive strength of PF before high-temperature heat treatment was shown in Fig.5. The compressive strength of G/K-PF foams was significantly better than that of K-PF foams, since the force was applied on both backbones of PF and glass fiber. While densities of G/K-PF foams were much higher than that of K-PF foams, the average specific compressive strength of G/K-PF foams was lower than K-PF foams. For K-PF foams with relatively low proportion of kaolin powder (K-PF/10wt%, K-PF/20wt% and K-PF/30wt%), the powder could disperse well in the mixture before foaming thus rendering even cell sizes, which was essential for foams to exhibit good mechanical properties. But for K-PF foams with higher amount of kaolin powder, their filler tended to aggregate, thus leading to big and uneven pores formed in PF. On the other hand, the specific compressive strength of K-PF foams were all lower than that of pure PF, since the kaolin powder's reinforcing effect could not catch up with its role of greatly increasing weights of PF. The mechanical properties of G/K-PF foams were all better than PF because there were several layers of glass fiber fabrics, which could obstruct cells from growing too big and uneven. Thus a large amount of cell walls and ribs would be produced to disperse the force. Of special note was that the compressive strength of G/K-PF/10wt% was lower than others. That was because that the viscosity of its prefoam mixture was low, which may led the powder precipitating on fabrics thus forming uneven cells. When adding filler to 40wt%, prefect viscosity of mixture was obtained, so the powder would suspend in it, which could help foams forming uniform cells. But for G/K-PF/50wt%, its filler were inclined to aggregate, so it began to form uneven pores and showed inferior mechanical behavior.

The compressive strength and specific compressive strength after high-temperature heat treatment were also tested in Fig.6. As stated above, PF with glass fiber and kaolin powder had better thermal stability, so compressive strength after high-temperature heat treatment of G/K-PF foams were higher than that of K-PF foams. But compressive strength of G/K-PF/0wt% was lower than K-PF/0wt%,
because without help of kaolin powder (acted as nucleating agent), pores would not become uniform enough among glass fiber fabrics. Analyzing data of K-PF, PF with lower content of kaolin powder had better thermal stability. That was because embedding kaolin powder to the backbone of PF could have a pinning effect on foams, thus increasing the strengthen of backbones and decreasing the damage of PF during burning process. But for K-PF/40wt% and K-PF/50wt%, they contained asymmetrical cells and incomplete resin network, making them difficult to resist the fire. As for G/K-PF foams after high-temperature heat treatment, foams which contained 40wt% of kaolin powder showed best mechanical behavior (highest specific compressive strength) in that it had most uniform cells. It could be seen that PF with powder and glass fiber showed excellent mechanical properties even after the burning process, thus they can be used as wall materials to protect buildings in the fire.

![Fig 5. Compressive and average compressive strength of PF before high-temperature heat treatment (a) G/K-PF foams; (b) K-PF foams.](image)

![Fig 6. Compressive and average compressive strength of PF after high-temperature heat treatment (a) G/K-PF foams; (b) K-PF foams.](image)

3.5. Analysis of thermal properties
To further investigate the thermal stability of modified PF, weights of PF were measured before and after high-temperature heat treatment. Weight loss of each foam was shown in Fig.7. Weight loss of G/K-PF was lower than that of K-PF, indicating thermal stability was enhanced with the help of the fabric. For G/K-PF/10wt% and G/K-PF/20wt%, they showed relative higher weight loss. The reason
was, as stated above, the filler could not disperse well in foams due to the low viscosity of prefoam mixture, which hampered the pinning effect of the filler. The G/K-PF/30wt% and G/K-PF/40wt% exhibited better thermal stability than G/K-PF/10wt% and G/K-PF/20wt%. That was because proper viscosity of mixture was obtained, making the filler scattered well in PF. Since the filler could serve as nucleating agent, cells would form evenly around the powder. So thicker walls and more ribs would be acquired, which would better stabilize the whole PF. As for G/K-PF/50wt%, it did not have even cell sizes but still show low weight loss. The reason was that its weight was mainly made up of filler, which would neither gasify nor decompose during high-temperature heat treatment.

![Fig 7. Weight loss rate of PF (a) G/K-PF foams; (b) K-PF foams.](image)

4. Conclusion

Kaolin powder facilitated PF to form even and small cells, leading to thicker wall ribs and good mechanical properties. Besides, the powder was embedded in backbones of PF, which could increase its mechanical strength and thermal stability. However, if adding a large proportion of the powder to PF, particles tended to aggregate and caused big cells inside the foam, which was detrimental for foam’s mechanical and thermal characteristics. On the other hand, after adding both fabric and the powder to PF, stress was applied on both backbones and the fabric, resulting to benign mechanical behaviors of the foam. Since glass fiber fabric hindered the gas from coming out, thermal stability of PF could be greatly improved. From IR results, both fabric and kaolin powder do not react with matrix.

References

[1] Xin W, Ehsan Naderi Kalali, Wan JT, Wang DY. Carbon-family materials for flame retardant polymeric materials[J], Progress in Polymer Science 2017; 69: 22-46.
[2] Jedediah B, Alvey, Jignesh Patel, Larry D, Stephenson. Experimental study on the effects of humidity and temperature on aerogel composite and foam insulations[J], Energy and Buildings 2017; 144: 358-371.
[3] Wang G, Wang C, Zhao J, Wang G, Park C, Zhao G. Modelling of thermal transport through a nanocellular polymer foam: toward the generation of a new superinsulating material[J], Royal Soc Chemistry 2017; 9: 5996-6009.
[4] Allameh-Haery H, Kisi E, Fiedler T. Novel cellular perlite-epoxy foams: Effect of density on mechanical properties[J], Journal Of Cellular Plastics2017; 53: 425-442.
[5] Seung A Song, Youngmin Lee, Yeon Su Kim, Seong Su Kim. Mechanical and thermal properties of carbon foam derived from phenolic foam reinforced with composite particles[J], Composite Structures 2017; 173: 1-8.
[6] Hu LF, Wang ZZ, Zhao QL. Flame Retardant and Mechanical Properties of Toughened Phenolic Foams Containing a Melamine Phosphate Borate[J], Polymer-Plastics Technology And Engineering 2017; 56: 678-686.
[7] Yang C, Zhuang ZH, Yang ZG. Pulverized polyurethane foam particles reinforced rigid
polyurethane foam and phenolic foam[J], Appl Polym Sci, 2014;131(1): 527.

[8] Smith, S. B. Thermocell Development Ltd. U.S. Patent 4,390,641, 1983.

[9] Zhang L., Yilmaz ED, Thomsen JS, Rauhe JC, Pyrz R. MWCNT reinforced polyurethane foam: processing, characterization and polydispersity of mechanical properties[J], Compos Sci Technol 2011;71:877–84.

[10] Chen L, Schadler LS, Ozisik R. An experimental and theoretical investigation of the compressive properties of multi-walled carbon nanotube/poly(methyl methacrylate) nanocomposite foams[J]. Polymer 2011;52:2899–2909.

[11] Desai A, Auad ML, Shen H, Nutt SR. Mechanical behavior of hybrid composite phenolic foam[J]. J Cell Plast 2008;44:15–36.

[12] Jeffrey G. Lundin, Christopher L. McGann, Grant C. Daniels, Benjamin C. Streifel, James H. Wynne, Hemostatic kaolin-polyurethane foam composites for multifunctional wound dressing applications[J]. Materials Science and Engineering: C 2017; 79: 702-709.

[13] V. Ferrari, E. Disegna, E. Dellacassa, A. Comiberti. Influence of timing and intensity of fruit zone leaf removal and kaolin applications on bunch rot control and quality improvement of Sauvignon blanc grapes, and wines, in a temperate humid climate[J], Scientia Horticulturae 2017; 223: 62-71.

[14] Ning Li, Tiesen Li, Haiyan Liu, Yuanyuan Yue, Xiaojun Bao, A novel approach to synthesize in-situ crystallized zeolite/kaolin composites with high zeolite conten[J], Applied Clay Science 2017; 144: 150-156.

[15] Fernando de Oliveira, Cristina Gomes da Silva, Luiz A. Ramos, Elisabete Frollini, Phenolic and lignosulfonate-based matrices reinforced with untreated and lignosulfonate-treated sisal fibers[J], Industrial Crops and Products 2017; 96: 30-41.