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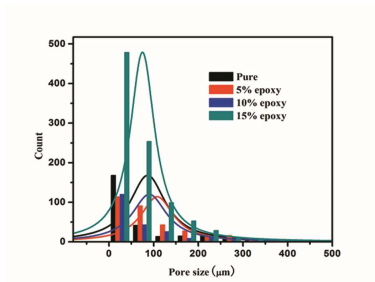
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## A Simple Method Preparation and Characterization of Epoxy Reinforced Microporous Phenolic Open-Cell Sound Absorbent Foam

Rui Gong<sup>1</sup>, Qian Xu<sup>1</sup>, Yineng Chu<sup>2</sup>, Xingyue Gu<sup>3</sup>, Jie Ma<sup>3</sup>, Ruihai Li\*

The cell distribution of open-celled phenolic foams with different contents of epoxy (0 wt %, 5 wt %, 10 wt %, 15 wt %).



## A simple method preparation and characterization of epoxy reinforced microporous phenolic open-cell sound absorbent foam

Rui Gong<sup>1</sup>, Qian Xu<sup>1</sup>, Yineng Chu<sup>2</sup>, Xingyue Gu<sup>3</sup>, Jie Ma<sup>3</sup>, Ruihai Li\*

<sup>1,2,3</sup>Department of Polymer Science and Engineering, Sichuan University, Chengdu, 610065, China

\*State Key Laboratory of Polymer Materials Engineering of China, Chengdu, 610065, China

**Abstract:** A series of micro-porous phenolic open-cell sound absorbent foams reinforced by epoxy resin were fabricated by physical foaming method. The compound emulsifiers consisting of anionic and non-ionic surfactants were physical blended at high speed with modified resols, foaming agent and mixed acid curing agent. The viscosity, surface tension, gel permeation chromatography (GPC) were characterized. Fabricated foams were characterized for pore size distribution, water absorption, sound absorption, mechanical and thermal properties. Surface tension and porosity analysis demonstrated that anionic surfactant, sodium dodecyl sulfonate (SDS) promoted the formation of homogeneous micro-pores. And the open cell porosity reached up to 90%. The open-celled pore structure and cell size distribution revealed by Scanning electron microscopy (SEM) demonstrated that more homogeneous and smaller open cells existed with increasing dosage of epoxy. And the sound absorption properties were increased significantly when adding the epoxy resin, even can reached about 95%. The micro-pore and cell-distribution controlled by the content of epoxy resin and the ratio of SDS/tween-80, greatly improved the mechanical strengths of phenol-formaldehyde resin (PF).

**Keywords:** open-cell structure; porosity; ionic surfactant; thermal property; water and sound absorption.

### INTRODUCTION

Open-celled microcellular foam polymer materials, because of their unique interconnected micro-pore structure, possess a wide range of properties well suited for many micro-porous material applications.<sup>1</sup> The open-celled structure allows particles, fluids and sound, gas to flow through the material, resulting in a product that can be used as a filter or membrane, catalyst supporters, drug delivery materials and so on.<sup>1-2</sup>

Currently, studies on porous functional polymer materials are gradually becoming a research hotspot.

Up to now, there exists to be four main ways to prepare open cell plastics and foams: thermally induced phase separation, supercritical fluid, monomer polymerization and precipitation with a compressed fluid anti-solvent precipitation.<sup>3-4</sup> Besides, previous researchers have also developed new techniques (such as block copolymer, polymer nanometer-composites foaming methods) to obtain polymers with open cell structure.<sup>5-6</sup> In addition, over the past decades, numerous researches about PF mainly focus on closed cell insulation materials. There are few studies about open cell phenolic foam which is produced from resols at medium-low temperature under atmospheric

pressure, using simple physical foaming method. Although, it has been merely reported two methods for the preparation of open cell phenolic foams so far: supercritical fluid foaming from novolacs.<sup>7</sup> and open cell carbon foams prepared by phenolic foam as precursor.<sup>8</sup> Therefore, it is necessary to invent such new practical and simple method to manufacture open cell polymers with excellent performances.

As for epoxy resin, it also possesses many excellent advantages of low shrinkage, chemical resistance and superior mechanical properties.<sup>9-11</sup> Furthermore, it is acknowledged that the epoxy group can occur to react with hydroxyl in resol via etherification.<sup>10</sup> Given excellent mechanical performance of epoxy resin and the reaction mechanism, epoxy resin of adaptive viscosity is taken into consideration as a reinforced functional agent. Because it is fine open-celled microcellular structure of phenolic foam and combined performance of epoxy that can make the composite foam possess many mutual excellent properties including low toxicity and smoke, flame retardancy, high strength and dimensional stability, chemical resistance. The prepared foams with superior compressive strength and flexural properties possess considerable pore structure, good properties of filtration and water permeability and low production cost character. So these combined performances and low production cost character of open cell phenolic foam make it very versatile in some applications, such as: sand control in oilfields, chemical filtration and separation, sewage treatment, microfiltration membranes, adsorption materials and so on. Thus, the application prospect of open cell phenolic foams will be promising. In addition, in the last several decades,

the use and variety of available specialized sound-absorbing materials has increased greatly.<sup>12</sup> There are many studies on acoustic insulation materials, such as polyurethane and Polyethylene terephthalate foams, and can do a lot of sound-absorbing foam green and recyclable.<sup>13-15</sup>

In our study, we developed a new simple physical foaming approach to prepare epoxy modified micro-porous phenolic open-cell foam with resols, differing from previous modification of directly physical blending foaming method. It should be noted that we innovated to use different anionic and nonionic compound surfactants<sup>16</sup> as our emulsifiers and mixed acid curing catalyst. And phenol-formaldehyde resol modified by epoxy resin was synthesized. And reaction between epoxy and resol was catalyzed with suitable sodium hydroxides solution. In addition, we also mixed epoxy resin with pure resol directly, followed by foaming with our method for comparison, just only to find that it failed to foam with open porous structure. A series of pre-polymer with different dosages of epoxy resin were synthesized. And the viscosity of modified resols was measured at 0.6 rpm, 1.5 rpm, 3.0 rpm and 6.0 rpm each different shear rate. The influence of different ionic surfactants on emulsification effect was characterized by surface tension test. Gel time measurements were carried out to assess the curing reaction activity and thermal behavior of resol resins. Gel permeation chromatography (GPC) was used in the determination of average molar masses and polydispersity index, as a function of the degree of condensation of the resin. Finally, open-celled microcellular foams with various dosage of epoxy were prepared by simple physical foaming method. The bulk

density, solids content of resins and thermal conductivity were measured. The open cell porosity and water absorption were tested, respectively. The microstructure of cells and the physical phase distribution of modified resol were observed by SEM. Moreover, the compressive and flexural properties of open-celled microcellular phenolic foam were characterized.

## EXPERIMENTAL

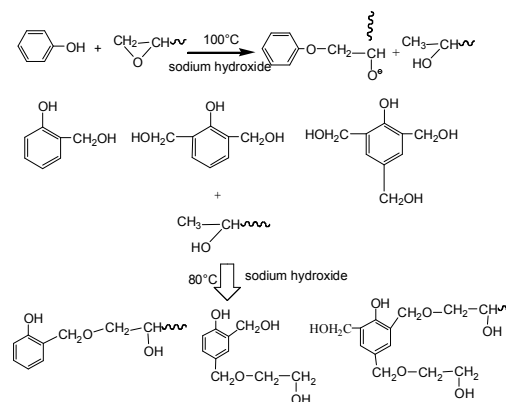
### Materials

Phenol ( $\geq 99\%$ ), paraformaldehyde ( $\geq 95\%$ ) and sodium hydroxides (analytical grade) were provided by Chengdu Kelong Chemical Regents Factory, China. Hydrochloric acid, phosphoric acid, toluene-p-sulfonic acid, acetic acid, tween-80 (polyoxyethylene sorbitan monooleate) and sodium dodecyl benzene sulfonate (SDBS), sodium dodecyl sulfate (SDS<sup>\*</sup>), sodium dodecyl sulfonate (SDS) (all were analytical grade) were also purchased from Chengdu Kelong Chemical Regents Factory, China. Cyclopentane ( $\geq 95\%$ ) was provided from Chengdu Aike Chemical Regents Factory, China. Diglycidyl ether of bisphenol-A (DGEBA) type epoxy resin (trademark: E-51:WSR618) was purchased from Nantong Xingchen Synthetic Material Co., Ltd. (epoxy value=0.48-0.54 eq/100g; viscosity (40°C)  $\leq 2500$  mPa.s).

### Synthesis of the Modified Resol

In this study, the modified resols were condensed in a 250 ml flask equipped with a stirrer, a external cooling condenser and internal heating units. Epoxy modified resol in this study was prepared by the polymerization of phenol and formaldehyde (in a mole ratio of  $R = [F]/[P]=1.8$ ) with a given amount of modifier epoxy resin at 80°C for 3 h, using sodium

hydroxide solution as catalyst.<sup>17-18</sup> The detailed synthesis procedure was as follows: firstly, a given amount of molten phenol and 20% sodium hydroxide solution (the amount of its substance was 0.123 mol) were added into three-necked flask stirred for 15min. Then a certain amount of epoxy was added into mixed solution with stirring. When the temperature reached 80 °C, the paraformaldehyde divided into four equivalent parts was added every 10 minutes. The process lasted for 3 hours and the resol-type pre-polymer was obtained.<sup>17-19</sup> The mechanism of chemical modification of epoxy-modified phenol and resol was revealed in Scheme 1.



**Scheme 1.** The synthesis route and mechanism of epoxy-modified phenol and resol.

### Preparation of the High Strength Micro-Porous Phenolic Open-Cell Foam

The choice of surfactants, foaming agents and curing agent directly affects the result of the open-cell phenolic foam. It is particularly important to select a suitable surfactant, a foaming agent and a curing agent. Anionic surfactants are conducive to the formation of the open-cell structure, while non-ionic surfactants are

conducive to the formation of closed cell structure. Two surfactants complex mixed-use, are effective to form the phenolic foam of open-cell structure of high porosity. The select of foaming agent is important in the course of microporous phenolic open-cell foam, because you must to give full consideration to its boiling point and its resin matrix compatibility. Liquid foaming agent dispersed degree and vaporization rate speed of escape in the resin, which is very important for the formation of an open cell structure. After comparison of dichloromethane, petroleum ether, cyclopentane and other types of foaming agents, it found that the choice of the boiling point of 49.5 °C cyclopentane made out of a good open cell structure and excellent performance foam. So at last finalize the cyclopentane as the foaming agents. The curing reaction between active methylol crosslinking of the resole resin need acid as a catalyst. Acid can accelerate the condensation reaction of the resin molecules, exothermic heat of reaction prompted a sharp foaming agent vaporization, gas overflow of the resin droplets and forming foaming resin, the resin is cured. The catalyst is also a resin curing agent. Selection and the amount of curing agent should follow the principle of the cured resin and foaming rate that matches, and the curing reaction proceeds at a relatively low temperature. When a strong acid as a curing agent, curing crosslinking rate faster than the rate of foaming, and acid corrosive mold large, strong acid and the medium-strong acid as a mixed curing agent, not only can reduce the curing rate and a foaming agent to match, but also to reduce the mold corrosion. By contrast, hydrochloric acid, phosphoric acid, methyl sulfonic acid, etc. for different curing agents, found that by hydrochloric acid and phosphoric acid complex,

the foaming speed and curing speed can control in the appropriate range, can achieve better performance of the microporous phenolic open-cell foam.

Micro-porous phenolic open-cell foam samples were fabricated using our proprietary technology. The foaming formulation was typically comprised of epoxy modified resol 100 Phr, a certain ratio of anionic (SDS, SDBS, SDS') and nonionic (tween-80) surfactants compound emulsifiers 4 Phr, mixed acid catalyst 10 Phr and appropriate amount of cyclopentane. Our preferred foaming condition for open cell phenolic foam was prepared by homogeneously blending modified phenolic resol, compound emulsifier, foaming agent cyclopentane successively with high-speed mechanical mixer. Next the mixture was mixed with compound acid and stirred for 35 s quickly. Finally obtained viscous mixture was poured in preheated foaming mold immediately and cured in at 70 °C for about 30minutes, followed by foaming. Samples were cut precisely and used for mechanical testing.

## CHARACTERIZATION AND MEASUREMENTS

Viscosity tests of epoxy modified resols were carried out with a NDJ-8S digital viscometer (Shanghai Jinhai Instrument Co. china) at  $25 \pm 0.1$  °C, using the 2nd rotor, at different shear rate.<sup>20</sup>

Surface tension was investigated by a surface tension instrument (Krüss K100, Germany) at  $25 \pm 0.1$  °C. And resol/anionic and nonionic surfactant mixed solution of a certain equal concentration were prepared for testing.

The resin was characterized by GPC (HLC-8320 GPC gel permeation chromatography, Tosoh Corporation, Japan) with series chromatographic column. The resins were dissolved in filtered tetrahydro-furan (THF; 20 mg/mL), which was also used as an eluent. The sample size was 10uL, and the eluent rate was 0.6 mL/min. The measurements were made at 40 °C. The retention times were recorded. Nelson was used to calculate the number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ), as well as the polydispersity.

The micro-porous morphologies of the samples prepared were characterized on an INSPECTF scanning electron microscope (FEI Holand). Pore size and distribution of these samples were observed from the section surfaces of foam specimens. Samples were carefully cut from the freshly peeled flat surfaces using razor blade. Gold sputtering onto the sample surface was used to impart electrical conductivity. Also the dispersion of physical phase in resin matrix of modified resol and pure resol mixed with equal content of epoxy were observed by an INSPECTF scanning electron microscope (FEI Holand). Resol samples were fully dried under vacuum. And the distribution of phase in resol was observed from the surface of section. The statistical analysis of cell size and distribution is conducted through Image Pro Plus6.0 software.<sup>21-22</sup>

The thermal conductivity of these samples was measured by using thermal constant analyzer (Hot-Disk 2500-OT) at 293K. The size of all the samples was about 30 mm×30 mm×20 mm.

The bulk density was measured according to ISO 845:2006. Samples were prepared in 50 mm square 5mm thick. The result was calculated as follows:

$$\rho = m/v$$

Where  $\rho$  is the apparent density ( $\text{kg/m}^3$ ),  $m$  is the mass of sample (Kg), and  $v$  is the volume of the sample ( $\text{m}^3$ ).

The water absorption of open-celled phenolic foams was investigated in accordance with ISO 2896:2001. And the porosity of open cell PF was tested with the immersion method according to GB10799-89. The test specimens were used with the dimensions of 50×50×20  $\text{mm}^3$ . Specimens were soaked completely in distilled water for 24h, and the surface water of foam was wiped dry with absorbent paper, monitoring the weight changes of samples in the air and water respectively to measure its water absorption and porosity. Parallel tests were made at least three times. The determination of water absorption and porosity of foams were calculated by the following formula.<sup>23</sup>

$$\text{water absorption (\%)} = [(m_2 - m_1) / m_1] \times 100\%$$

Where  $m_1$  is the mass of dry phenolic foam,  $m_2$  is the mass t of soaked phenolic foam after 24h

$$\text{Porosity} = [(G'_2 - G'_1) \rho_L] / [(G'_2 - G_3 + G_4) \rho_{me}]$$

Where  $G'_1$  is the weight of soaked saturated phenolic foam in the air,  $G'_2$  is the the weight of soaked phenolic foam after 24h,  $G_3$  is the total weight of soaked phenolic foam, trays and weight after 24 h in the water,  $G_4$  is the weight of trays and weight in the water,  $\rho_L$  is the density of water,  $\rho_{me}$  is the density of saturated medium.

The water permeability test was done to measure the volume of permeated water to evaluate its permeable effect. The weight of the sample before and after was measured on a balance. Thickness of open cell phenolic

foam was 20 mm. Samples were flattened on top of the 50ml beaker for 15 min since water was dropped on the upper of the foams.

The Sound absorption properties of the samples were characterized on an SW466-type wave tube provided by the Sound Power Technology Co., Ltd. Beijing prestige. Foam samples were cut into cylindrical with diameter of 78mm, a thickness of about 20 mm. And test frequency range from 400 to 2500 Hz.

The compressive tests and bending properties were carried out according to ISO 844:244 and ISO 1209-2:2004, respectively, using an (AGS-J 10KN) Universal Testing Machine under ambient conditions. At least five specimens for each material were tested to obtain average values. The rate of compression was controlled by 10% of the initial thickness, until compressed to 85% of the initial thickness. And the bending span was  $100 \pm 1$  mm. And the density of foams was calculated according to the dimensions value of test species.<sup>24</sup>

## RESULTS AND DISCUSSION

### Viscosity Analysis

Fig. 1 presents the relationship between the viscosity of pre-polymer resols and content of modifier epoxy measured at shear rate of 3.0 rpm. With the dosage of epoxy increasing, the viscosity of pre-polymer decreased at the content of 5 wt % and then gradually increased from 5 wt % to 15 wt %.

There are two main factors affecting the viscosity: molecular weight and molecular weight distribution. The relative molecular weight of epoxy resin is higher than that of pre-polymer. So the introduction of higher

molecular weight epoxy resin will lead to increase of viscosity. With the dosage of epoxy increased, meanwhile the molecular weight distribution also changed, leading to the change in the viscosity of the resin system. Furthermore, the increase of viscosity in a certain range is also beneficial to inhibit the diffusion of the surfactant molecules, which causes to the increase of surface elastic effects, resulting in improvement of the stability of bubbles. What is more, there are still another factor accounting for the decreasing trend of viscosity at the content of 5% -10% wt. The graft structure side chain, which is the occurrence reaction between the hydroxyl group, methylol and epoxy group via etherification, can make mean square radius of gyration alter longer and make molecular motion space larger, resulting in the decrease of viscosity of modified resol. Additionally, appropriate amount of modifier epoxy also may break the intermolecular hydrogen bonds between polymer molecules, leading to the reduction in viscosity too. The reduction in viscosity indicated that the addition of suitable dosage of modifier epoxy resin could reduce viscosity of pre-polymers effectively, affording optimal foaming viscosity for preparing open-celled porous phenolic foam compared to pure resol. Once further increased, excessive unreacted epoxy in the matrix resin increased systemic viscosity.

In addition, different added amount of modifier epoxy showed the residual phenol and formaldehyde of resol were not the same, too. The results presented in Fig. 4 show that the more epoxy added, the less residual phenol and formaldehyde obtained. Besides, we also conducted a contrast trail (10% content of epoxy mixed with pure resol directly). Its residual phenol was 2.60%, which was not the same with 10



wt % epoxy modified resol, either. Also when the content of epoxy reached 10 wt %, residual formaldehyde was at the lowest level. Compared to pure resol, residual phenol and formaldehyde of modified resol reduced in various degrees. It is also indirectly demonstrated that phenol or methylol of resol occurred to react with epoxy group. This also proved that epoxy modified resol indeed decreased the content of free phenol and residual formaldehyde.

#### Surface Tension Analysis

It is a virtually complex procedure containing nucleation, growth, stability and solidification of bubbles during the foaming progress. In the foaming progress bubbles have gone through four different stages: bubble nucleation, bubble growth, bubble collision, bubble combination. And the effect of SDS as anionic surfactant is to promote post-foaming bubble collision and merger. Actually, during later foaming progress, anionic surfactant (SDS, a electrolyte ) might break resin droplets encapsulating cyclopentane and act as a demulsifier to make vaporizing cyclopentane escape outward gently from resin droplets. SDS increase can significantly improve the porosity and the number of micropores. The Moreover, the series of changes are closely associated with the surface properties of the phenolic resin solution and the emulsification of surfactants. Therefore, it is necessary to investigate the surface tension of resol emulsified with different percentage of compound surfactants to reveal the impact of surfactants on the surface properties of the resin solution. Surface tension curve of resol emulsified with different SDS content is shown in Fig. 2. The surface tension of resol decreases first in a certain content of SDS extent between 0% and 45%, and then gradually

increases with the increasing dosage of SDS. In the range of 45%-55%, the surface tension increases slowly. However, its surface tension increases sharply when the content of SDS exceeds 55%. This phenomenon can be explained by the following formula:

$$\Delta F = \nu \cdot \Delta A$$

$\Delta F$ -Change in the free-energy of the system;  
 $\Delta A$ -Change in the total interfacial area of bubbles in the system;  $\nu$ - Surface tension of the system.

According to above formula, when surface tension  $\nu$  decreases, it is bound to increase the surface area of the system  $\Delta A$  to make the free energy of the system maintain a constant value. And once  $\Delta A$  increased, numbers of bubbles could be formed and turned subtle rapidly. At the same time, the reduction of systemic surface tension can also prevent coalescence of generated bubbles and stabilize these bubbles. When the dosage of SDS exceeds 55%, bubble maybe start up to collision and connection, and when the content of SDS exceeded 67.5%, excessive SDS was deficiently dissolved in the resin for emulsification, which affected the stability of the system. Therefore, we could assume that initially, SDS played a role in making the bubbles combined and interconnected in the resin system. Until when the amount of SDS increased to a certain extent (67.5%), the function of SDS changed. Instead, it had some negative impact on the stability of tween80 in the system. At the same time, table 1 also records the influence of different anionic emulsifiers on surface tension, under the equal conditions of anionic emulsifiers/modified resol, the surface tension of resol emulsified with SDS remained least. Because compared to other anionic emulsifiers, SDS could be

better compatible with resol to make the surface tension of system decrease so as to stabilize the bubbles. That is the reason why we chose it as the anionic emulsifier. Besides, judging from table 1, although the modification of epoxy resin improved the surface tension of the system a little, once when the content of epoxy reached 10%, its surface tension reached lower than other percentage of epoxy. This is ascribed to the different increase of the systematic viscosity.

#### **Molar Mass Distributions and Molecular Weight**

The effect of the degree of condensation of the resol solution on number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ), and polydispersity index (PD) of the resin was determined using GPC. From Fig. 3 and table 2, the GPC curves of 10% content epoxy modified resol was slightly different from that of pure resol. The proportion of large molecules was higher. Both of the  $M_n$  and  $M_w$  values of modified resol (2) were slightly higher than that of pure resol (1), even the polydispersity value of (2) was lower than that of pure resol, indicating that modified resol exhibited narrow molecular weight distribution. Also referring to the viscosity curve, the viscosity of modified resol indeed increased as the masses ( $M_n$  and  $M_w$ ) increased. Predictably, the  $M_n$  and  $M_w$  Values of the resin indicate polymer condensation reactions and the formation of methylene bridge structures between the phenolic derivatives, thus confirming the results of analyses previously described.

#### **Cell Morphology and Distribution of Open Cell Phenolic Foam**

Cellular structure of the foam samples was studied by SEM. Fig. 5 shows the cell morphology of foam samples emulsified with 67.5% SDS and 32.5% tween 80 in four parts and increasing amount of modifier epoxy resin from 0 wt % to 15 wt % from left to right. The cell size and the effect of the addition of epoxy on the microstructure of open cell phenolic foams are examined. As is shown in Fig. 5, With the increasing addition of epoxy, the cell size of phenolic foams decreases generally, the distribution of pores turns uniform and concentrated. Besides, the micro-pores in foams are interconnected from each other, and the wall structure of pores also exist some interconnected smaller pores. By comparison, such micro-porous structure of phenolic foams showed a great contrast with that of pure open cell phenolic foam (pore structure was in the level of low open porosity and inhomogeneous). However, with the increase of dosage of epoxy, the pore size turns smaller, the distribution of pores turns more concentrated and homogeneous.

Fig. 6 is a pore size distribution of phenolic foams with different contents of epoxy, it is obvious to see, the pore size distribution of the four open-celled phenolic foam is substantially the Similar, the aperture concentrated in the aperture 200  $\mu\text{m}$  or less. And the number of pores rapid increase accompanied with the reduction in pore size and reached the maximum at size less than 50  $\mu\text{m}$ . In addition, the number of phenolic foam porous significantly increased as the dosage of epoxy reached 15 wt %, which is consistent with SEM image.

When the content of epoxy is 10 wt %, a large number of open cells with moderate pore size exist, showing more uniform distribution. Smallest size cells

with inhomogeneous pore distribution exist in the foams with the dosage of epoxy up to 15 wt %. When the content of epoxy reaches 5 wt %, not only the micro-pores of interconnected structure differs in size, but also its distribution is relatively un-concentrated than that of 10 wt % epoxy modified foam. As for pure open cell PF, the open cells exists less with inhomogeneous pore distribution. However, compared to pure PF, the micro-pores in modified foams is still more and relatively concentrated. Because anionic surfactant, sodium dodecyl sulfonate (SDS) which was better compatible with resol, could promote the formation of open cells and produce good homogeneous and moderate micro-pores. There are two factors leading to the existence of various pore size and distribution. Firstly, the increasing viscosity of pre-polymer contributes a lot to the effect of motion of molecule and the combination of bubbles. High viscosity makes the motion of molecule difficult and also delays coalescence of generated bubbles, which means the decrease of cure rate and the imperfection between curing and foaming rate, resulting in the impact on combination rate of adjacent cells during foaming process. Second, because of the steric hindrance, the difference of curing rate between molecules with grafted side chains and those without the side chains causes the difference in cell size and distribution too. Therefore, the results above demonstrate that with increase of epoxy in the range of 0% wt and 10% wt, the cell size turns more moderate and homogeneous, which is attributed to the increasing combination of cells. Besides, when the dosage of epoxy is up to 15 wt%, excessive epoxy caused some effect on the uniformity of cells.

Physics of phase equilibrium in resols were investigated to verify the successful modification of epoxy. As is observed from Fig. 7, chemical modification of resol exhibited more uniform and single phase, no dispersed phase. However, under the same condition, pure resol through physical blending with equal content of epoxy directly presented disordered dispersed-phase, because unreacted epoxy resin droplets were distributed in resin matrix randomly, emerging separated multi-phases with irregular dispersion. From phase analysis, we got the conclusion that modified resol could demonstrate more uniform single phase. The comparison from phase also proved successful modification of epoxy.

#### **Thermal Conductivity**

The effect of epoxy content on thermal conductivity of open cell phenolic foams are shown in Fig. 8. The interconnected open-celled pores structure reflected in the Fig. 5 provided effective thermal conduction channels. The more open-celled pores and higher open cell porosity, the larger thermal conductivity would be. In the case of thermal conduction and water absorption in particular, cell geometry, cell size and shape of openings between cells and cell wall thickness are some of the most influential structural characteristics that control the maximum amount of water absorption and thermal conductivity.

Judging from Fig. 8, with the dosage of epoxy increasing, the thermal conductivity increases first at 5 wt % content of epoxy and then decreases from 5-15 wt %. However, the thermal conductivity of epoxy modified PF still higher than that of pure PF. From Fig. 8, it can be clearly seen that open cell phenolic foam modified with 5 % wt content of epoxy had highest

thermal conductivity. And the highest open cell porosity could reach up to 91.209%. Also, open-celled phenolic foams had higher thermal conductivity than that of closed cell phenolic foam (0.02 W/m•K in thermal conductivity and 2 in water absorption). By experiments, we found out that SDS could be better compatible with the resin, compared to other anionic surfactants. The formation of open pores in PF could be ascribed to the reason that anionic surfactants promoted the formation of open-celled porous structure in the foam. Actually, during later bubble collision and combination progress, anionic surfactant (SDS, a electrolyte) might break resin droplets encapsulating cyclopentane and act as a demulsifier to make vaporizing cyclopentane escape outward gently from resin droplets, resulting in inter-connected open-celled pore structure.

#### **Water absorption, porosity and water permeability of phenolic foam**

For the sake of verifying the open porous structure of PF, a convincing experiment was carried out by testing whether it is pervious. And we used water absorption test to certify its open cell structure. From Fig. 9, it can be clearly seen that open cell phenolic foam emulsified with anionic surfactant (SDS) had higher water absorption than merely emulsified with non-ionic (tween-80) surfactant. Besides, table 3 and Fig. 10 presents the influence of related facts on water absorption and porosity and water permeability. It is acknowledged that water absorption increases with the improvement of open porosity, and water permeability is closely linked with the pore size and distribution. And water absorption capability of a porous medium is also directly related to fluid flow through the medium,

which is affected by the volume and shape of the pore structure. The formation of open micro-pores in PF and the difference in water absorption of open-celled and closed foam could be ascribed to the reason that anionic surfactants promoted the formation of open cell structure in the foam. Actually, during later foaming progress, anionic surfactant (SDS, a electrolyte) might break resin droplets encapsulating cyclopentane and act as a demulsifier to make vaporizing cyclopentane escape outward gently from resin droplets.

From the Fig. 10, we also could reach the conclusion that the water permeability gradually decreased with increasing content of SDS in compound surfactants, owing to the pore structure becoming smaller. The smaller of pore size, the more water will be remained in micro-pores. It also indirectly indicates the relationship between pore size and content of SDS: the pore size turned smaller with increasing ratio of SDS. Furthermore, as the SDS content increased, the water absorption also increased until the content of SDS reached 67.5%. When further continued to increase the content of SDS, it caused the adjacent cells to collapse and rupture. As the increasing numbers of ruptured bubbles, its water absorption decreased, instead. Thus we concluded that the more amount of SDS, the smaller pore diameter of cells in PF obtained, and more water would be retained inside the pores, resulting in higher water absorption. Therefore, this phenomenon was attributed to two factors: one was the impact of amount of anionic surfactant (SDS) on pore structure; the other was the mutual emulsification and demulsification effects of SDS anionic emulsifier. But once the proportion of SDS further exceeded 67.5%, cells would collapse to a large extent, owing to

insolubilization of excessive SDS in resin and the impact on foam curing progress. Noticeably, in the curing process, the curing rate of single strong acid catalyst was too fast, our method carried out mixture of strong acid (hydrochloric acid) and medium-strong acid(phosphate) compound curing agent was aimed at controlling and adjusting the curing rate so that it could suitably match the foaming rate. Under such suitable conditions, foaming-gas could escape outward from the resin droplets smoothly, leading to the cells in foam interconnected with each other and forming massive micro-porous structure. What is more, because of the reduced amount of hydrochloric acid, it also could decrease the corrosion of the mold in foaming process. . By comparison from table 3 and table 4, we can conduct that there exists to be three factors on porosity of PF: the ratio of hydrochloric/phosphoric, the amount of foaming agent and the content of epoxy. We found out that when the ratio of hydrochloric/phosphoric in volume was 7:3, the amount of blowing agent and epoxy content were 10% wt, the open cell porosity reached the maximum value of 88.430%. In addition, we also chose preferred different mixed acid type for comparison by water absorption and open cell porosity.

### Sound absorption properties

Fig.10 shows the experimental and theoretical sound absorption coefficients of specimens. The results are average of four samples. To access comprehensive the sound absorption performance of different samples, the average sound absorption is defined as the average of the sound absorption coefficient determined at octave bands with center frequencies 400, 500, 800, 1000, 1250, 1600 and 2500 Hz. Average absorption coefficient determines the overall acoustic performance

of the porous material and is shown in Fig. 11. It is obvious to observe that the sound absorption coefficient generally increases with frequency. The absorption coefficient of pure phenolic foam is the lowest, and the sound absorption coefficient is not more than 35% in the range 400-2500 Hz. While with the dosage of epoxy resin increasing, the sound absorption coefficient increased significantly, when the loadings of epoxy reaches 10 wt %, the acoustic sound absorption can reached 95% at high frequencies. According to the theory of their predecessors, the main mechanism of sound absorption can be summed up in the resonance absorption and the interface dissipation. When the sound wave propagates in the microcellular foam, sound travels through porous materials, sound energy is converted to thermal energy through friction between air and the inner walls of pores. This friction is largely captured by air flow resistivity, resulting in the sound attenuation, and thus achieved the purpose of weakening the reflected acoustic and sound absorption. As for the variation of sound absorption coefficient, it is ascribed to the cell size and distribution, open-cell porosity. Referring to the porosity and SEM analysis, it is clearly to verify the conclusion: The higher open-cell porosity and more uniform of cell distribution, the higher sound absorption coefficient would obtain. Besides, sound absorption coefficient of phenolic open-cell foam is also related to pore size, it will actually increase along with the pore size decreases.

### Mechanical Properties

Fig. 12 shows compressive and flexural strength of open cell phenolic foam modified with different loadings of epoxy resin. For PF/epoxy composite systems, it is obvious to know that epoxy resin can

significantly improve the mechanical strength of open cell phenolic foam. In Fig. 12, with increasing dosage of epoxy, the compressive strength increases at first and then ceases to increase then become progressively gently when the addition of epoxy changes from 10 wt % to 15 wt %. At the same time, the flexural strength of PF/epoxy increases gradually as the content of epoxy increases. When the epoxy loadings reached 10 wt %, modified open cell phenolic foam composites showed higher mechanical strengths (0.498 MPa in compressive strength, 0.78 MPa in flexural strength), compare to pure phenolic foam (0.09 MPa in compressive strength, 0.21 MPa in flexural strength), indicating that the incorporation of suitable amount of epoxy resin could improve the mechanical properties of the epoxy/PF composite systems. As for the improvement in mechanical, apart from the influence of foam microporous structure, we can also assume increased crosslink density (cause by increasing the epoxy concentration) causes the network stands to become shorter and have a chance to increases the strength.<sup>25</sup>

It is well known that the strength of open cell phenolic foam depends on foam structure, such as the size of pore, the uniform distribution of pore structure, the toughness of cell wall and the ratio of open cell. During compressive loading, open pores help scatter and absorb the stress and energy for keeping the integrity of skeleton, which may ensure the material high strength. Furthermore, the addition of epoxy could make open pore structure more uniform in distribution and smaller in size. Also, it can be seen in Fig. 12 that the strength increases seldom when the epoxy content increases to 10 wt %, indicating that there was an optimum addition quantity of modifier to improve the

flexural and compressive strength of open cell phenolic foam in our experiments. What's more, when the content of the epoxy resin exceeds 15%, the resin viscosity is too high and resulting in lower liquidity, that will emerge considerable of non-uniform cell structure and a gradual increase of the collapse of the holes, and resulting in the reduction in the mechanical properties. Besides, compared the table 4 and the figure 12, it indicated that the bulk density of open cell PF increases continuous with the increasing dosage of epoxy resin, but the mechanical strengths did not always increases. And there was an optimum addition quantity of modifier to improve the flexural and compressive strength of open cell phenolic foam in our experiments. So we can draw the following conclusions: the amount of epoxy responsible for higher mechanical strengths while not the foam density, In addition, the influence of the content of the epoxy resin was affect by the open cell porosity, the size and the distribution of microporous.

## CONCLUSION

In this work, a simple and effective route for obtaining high strength micro-porous phenolic open-cell foam modified by epoxy resin with simple physical foaming method has been described. We successfully synthesized modified resols with different loadings of epoxy. The effects of epoxy on the micro-structure of open-cell porous phenolic foams and properties of pre-polymer were studied. The porous structure, water absorption, mechanical properties and so on of open-cell phenolic foams and curing behavior and molar weight, viscosity of resols were characterized, respectively.

The  $M_n$  and  $M_w$  values of modified resol with narrow molecular weight distribution increased higher than that of pure resol. The addition of epoxy increased the viscosity of pre-polymer which was obvious when the dosage of epoxy was over than 5 wt %. Surface tension analysis also revealed the emulsification effect of anionic surfactants, i.e., SDS could be better compatible with resol to make the surface tension of system decrease so as to stabilize the bubbles. Besides, the micro-pore structure and distribution inferred from the water absorption, porosity, water permeability and morphology of micro-pores, demonstrate that when the ratio of SDS in four parts compound emulsifier is in the range of 65%-67.5%, the amount of foaming agent cyclopentane reaches 10%, and the content of epoxy resin reaches 10%, the mixed acid of hydrochloric/phosphoric with the ratio of 7:3 in volume, the pore structure is more homogenous dispersed with moderate size. Water absorption, sound absorption properties and thermal conductivity also increase with the improvement of open cell porosity, the conductivity of 5 wt % epoxy modified phenolic foam exhibits the highest thermal conductivity and open cell porosity 91.209%, When the content of epoxy is 15 wt %, the highest water absorption reached up to 2.918. And with the dosage of epoxy resin increasing, the sound absorption coefficient increased significantly, even the acoustic sound absorption can reached 95% at a higher frequency. Besides through the SEM results, the pore size and distribution of foams would turn smaller and more homogenous with increasing content of epoxy resin. As to the mechanical properties, the compression and bending results show the incorporation of 10% content of epoxy can improve the bending strength of Epoxy/PF system at maximum extent by 2.71, increase

the compressive mechanical performance by 4.53, this is ascribed to the reason that open micro-pores help scatter and absorb the stress and energy for keeping the integrity of skeleton, which may ensure the material high strength.

## References

1. Z. A. Van, J. J. Williams, *Polym.*, 1986, **5**, 123-140.
2. D. Doermann, J. F. Sacadura, *J. Heat Transfer.*, 1996, **118**, 88-93.
3. J. H. Auber, R. L. Clough, *Polym.*, 1985, **26**, 2047-2054.
4. P. W. R. Raj, M. Sasthav, H. M. Cheung, *J. Appl. Polym. Sci.*, 1993, **47**, 499-513.
5. V. K. Rangari, T. A. Hassan, Y. X. Zhou, H. Mahfuz, S. Jeelani, and B. C. Prorok, *J. Appl. Polym. Sci.*, 2007, **103**, 308-314.
6. J.-N. Yang, P. Li, *J. Rein. Plastics. Compos.*, 2015, **34**, 534-546.
7. S.-W. Lei, Q. Guo, D.-Q. Zhang, J.-L. Shi, L. Liu, X.-H. Wei, *J. Appl. Polym. Sci.*, 2010, **117**, 3543-3550.
8. S.-W. Lei, Q. Guo, J.-L. Shi, L. Liu, *Carbon.*, 2010, **48**, 2644-2646.
9. D. Puglia, L. B. Manfredi, A. Vazquez, J. M. Kenny, *Polym. Degrad. Stab.*, 2001, **73**, 521-527.
10. M. L. Auad, L.-H. Zhao, H.-B. Shen, S. R. Nutt, U. Sorathia, *J. Appl. Polym. Sci.*, 2007, **104**, 1399-1407.
11. J. P. Pascault, R. J. J. Williams, *Epoxy Resin*, 2010, WILY-VCH Verlag GmbH & Co.K, .
12. P. A. Jorge, J. C. Malcolm, *Sound. Vibra.*, 2010, **44**, 12-17.
13. R. D. Rey, J. Alba, P. A. Jorge, V. J. Sanchis, *Appl. Acoust.*, 2012, **73**, 6-7.
14. X. Sagartzazu, N. L. Hervella, J. M. Pagalday, *Arch. Comp. Meth. Eng.*, 2008, **15**, 311-342.
15. J.-H Lin, C.-M Lin, C.-C Huang, C.-C Lin, C. T. Hsieh and Y.-C Liao, *J. Compos. Mater.*, 2010, doi: 10.1177/0021998310381438.
16. Pool field Yihong JP. 1983, Pat.5876432.
17. S. J. A. Kumar, K. S. Ahmed, *J. Rein. Plastics. Compos.*, 2013, **32**, 1370-1379.
18. J. Song, Y. Zhang, Y.-J. Liu, *Rsc. Adv.*, 2015, **5**, 203734-20740.
19. A. Aierbe, J. M. Cheverria, C. Riccardi, *Polym.*, 2002, **43**, 2239-2243.
20. B. D. Park, B. Riedl, E. W. Hsu, S. Jack, *Polym.*, 1999, **40**, 1689-1699.
21. S. R. Dhakate, K. M. Subhedar, B. P. Singh, *Rsc. Adv.*, 2015, **5**, 43036-43057.
22. R. Lin, L. Fang, X. Li, Y. Xi, S. Zhang, P. Sun, *Polym. J.*, 2006, **38**, 178-183.
23. M.-C. Li, X. Ge, U. R. Cho, *Macromol. Res.*, 2013, **21**, 793-800.
24. Y. Yang and J. He, *Polym. Compos.*, 2014, doi: 10.1002/pc.23066.
25. X. Ge, M. Li, and U. R. Cho, *Polym. Compos.*, 2014, doi: 10.1002/pc.23080.



### Figure Captions

**Fig. 1** Viscosity of pre-polymer measured at, 3.0 rpm shear rate with different contents of epoxy.

**Fig. 2** The influence of SDS contents on surface tension.

**Fig. 3** GPC curves of the resins: (1) the pure resol; (2) the epoxy-modified resin.

**Fig. 4** The amounts of residual formaldehyde and methylol index in various contents of epoxy modified resols.

**Fig. 5** SEM images (100  $\mu\text{m}$ ) of open-celled phenolic foams with different contents of epoxy (1-0 wt %, 2-5 wt %, 3-10 wt %, 4-15 wt %).

**Fig. 6** The cell distribution of open-celled phenolic foams with different contents of epoxy (0 wt %, 5 wt %, 10 wt %, 15 wt %).

**Fig. 7** SEM micrograph of modified resol with 10% content of epoxy (1); pure resol physical mixed with 10% content of epoxy directly. (2).

**Fig. 8** The thermal conductivity curves of open-celled phenolic foams emulsified with equal 65% SDS and 35% tween 80 in 4 parts and modified with different content of epoxy.

**Fig. 9** The relationship of modified foams between the water absorption and the content of epoxy (a: emulsified by 100% tween 80; b: emulsified by 67.5% SDS and 32.5% tween 80).

**Fig. 10** Effect of different content of SDS on water absorption and permeability.

**Fig. 11** The sound absorption coefficient of phenolic open-cell foams with different contents of epoxy (0 wt %, 5 wt %, 10 wt %, 15 wt %).

**Fig. 12** Compressive and flexural strength of Epoxy/PF systems modified with different content of epoxy with equal ratio of SDS=67.5%, tween 80=32.5% in 4 parts.

## Tables

**Table 1.** Surface tension of different anionic emulsifiers

<i>Samples</i>	<i>60%SDBS/40%tween 80</i>	<i>60%SDS/40%tween 80</i>	<i>60%SDS'/40%tween 80</i>	
<i>Surface tension(mN/m)</i>	30.47	29.60	30.71	
(SDBS-sodium dodecyl benzene sulfonate; SDS'-sodium dodecyl sulfate; SDS-sodium dodecyl sulfonate )				
<i>Samples</i>	<i>Pure resol</i>	<i>5%epoxy resol</i>	<i>10%epoxy-resol</i>	<i>15%epoxy-resol</i>
<i>surface tension(mN/m)</i>	24.59	30.81	29.47	30.70

**Table 2.** Average molar mass ( $M_n$  and  $M_w$ ), and Polydispersity index (PD) values of pure resol and 10 % content of epoxy E51 modified resol.

<i>Sample</i>	<i>number-average molecular weight</i> $M_n$ (g/mol)	<i>weight-average molecular weight</i> $M_w$ (g/mol)	<i>Polydispersity index, PD</i>
<i>Pure resol</i>	254	405	1.594
<i>Epoxy-modified resol</i>	307	432	1.408

**Table 3.** Porosity and water absorption data of different ratio of hydrochloric/phosphoric in volume and different amount of foaming agent (the amount of epoxy was 15 wt %)

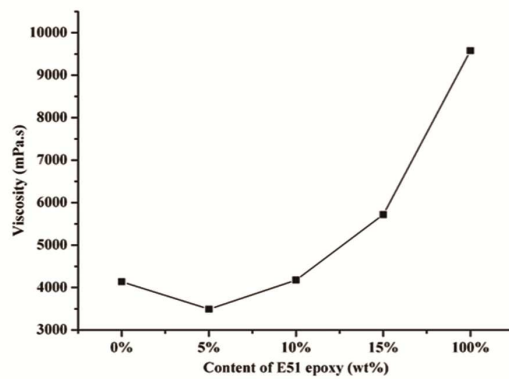
<i>Different Ratio of hydrochloric/ phosphoric in volume (10 parts curing agent)</i>	<i>Porosity of open cell PF</i>	<i>Water absorption</i>
<i>6:4</i>	85.658%	0.538
<i>7:3</i>	88.430%	2.918
<i>8:2</i>	88.019%	2.008
<i>9:1</i>	84.237%	2.631
<i>10:0</i>	81.830%	1.953

<i>Different amount of foaming agent(in equal ratio 9:1 of mixed acid 10 parts curing agent)</i>	<i>Porosity of open cell PF</i>	<i>Water absorption</i>
8%	83.063%	2.422
10%	88.430%	2.918
12%	82.665%	2.079

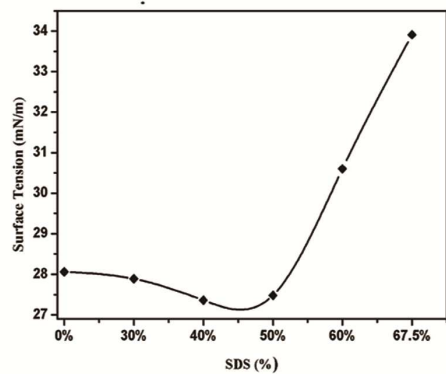
**Table 4.** Porosity, bulk density and water absorption data of different amount of epoxy resin

<i>Sample no.</i>	<i>Pure PF</i>	<i>5% epoxy-PF</i>	<i>10% epoxy-PF</i>	<i>15% epoxy-PF</i>
<i>Water absorption</i>	2.0272	2.218	2.251	2.918
<i>Open cell porosity</i>	89.123%	91.209%	90.235%	88.430%
<i>Bulk Density (Kg/m<sup>3</sup>)</i>	111.79	157.39	223.37	235.51

## Figures



**Fig. 1** Viscosity of pre-polymer measured at, 3.0 rpm shear rate with different contents of epoxy.



**Fig. 2** The influence of SDS contents on surface tension.

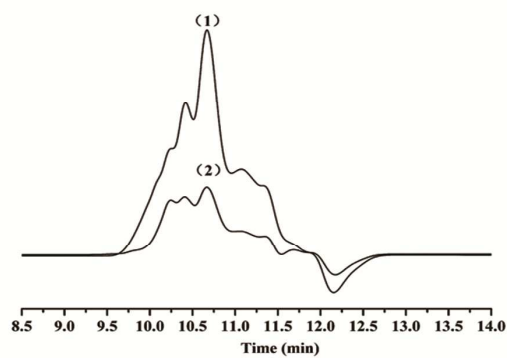


Fig. 3 GPC curves of the resins: (1) the pure resol; (2) the epoxy-modified resin.

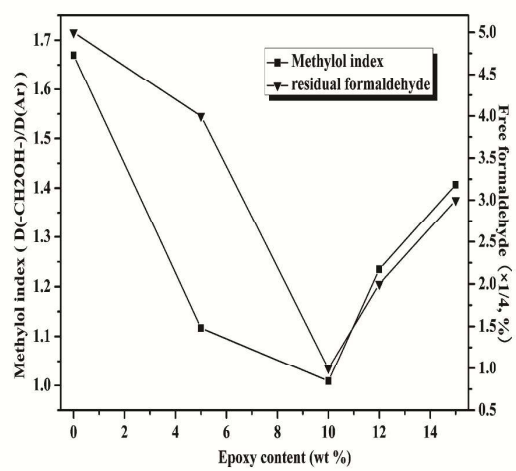
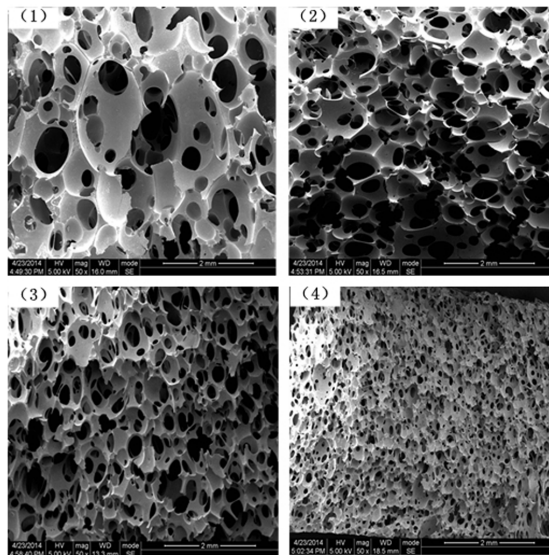
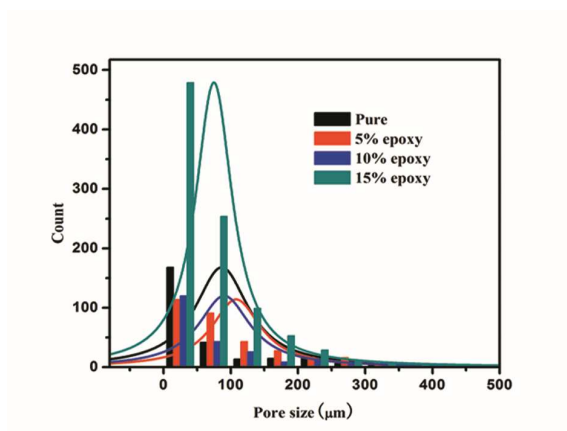


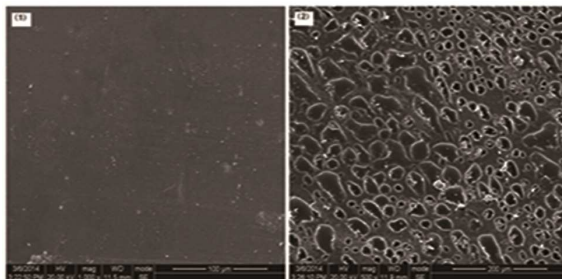
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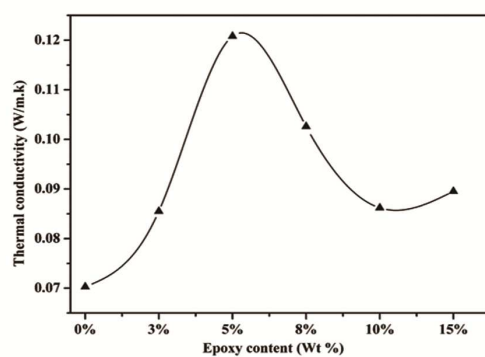
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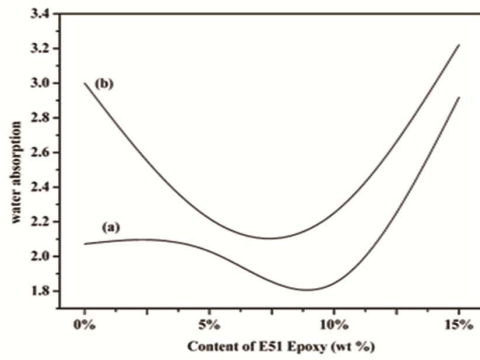
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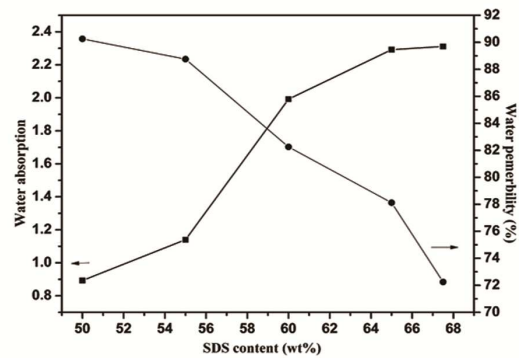
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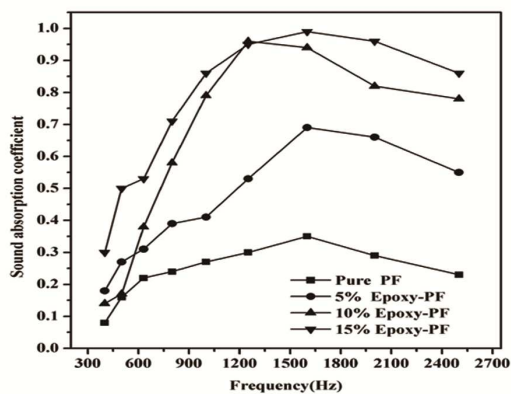


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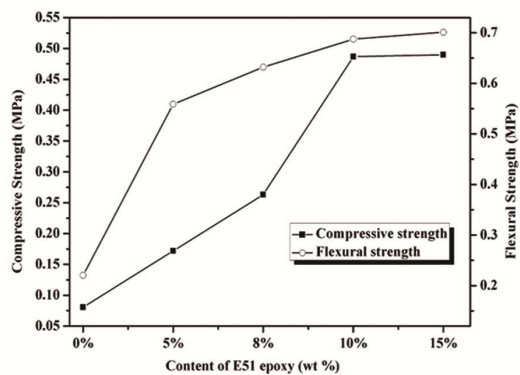


**Fig. 10** Effect of different content of SDS on water absorption and permeability.



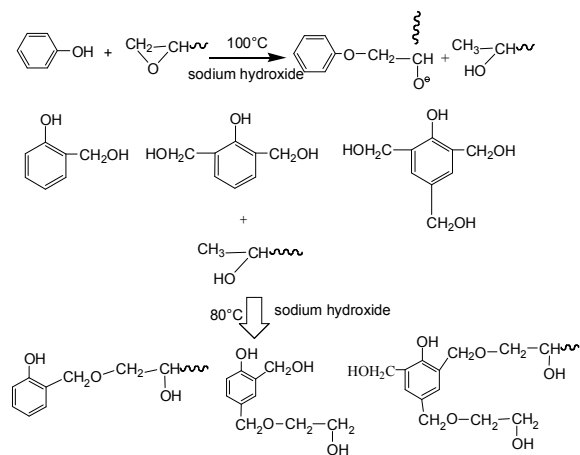


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**Fig. 12** Compressive and flexural strength of Epoxy/PF systems modified with different content of epoxy with equal ratio of SDS=67.5%, tween 80=32.5% in 4 parts.

## Scheme



**Scheme 1.** The synthesis route and mechanism of epoxy-modified phenol and resol.