

Preparation and Properties of Composites Based on Melamine-Formaldehyde Foam and Nano-Fe₃O₄

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ABSTRACT: In this work, a novel melamine-formaldehyde-Fe₃O₄ foam was prepared from a mixture containing melamine-ethanolamine-formaldehyde resin, melamine-glycol-formaldehyde resin and carboxylated Fe₃O₄ nanoparticles by microwave foaming method. The two resins were characterized by ¹³C-NMR, respectively. The structures of foams, mechanical and fire-retardant properties were experimentally characterized separately by scanning electron microscopy, universal testing machine, limit oxygen index, thermogravimetry-differential thermal analysis, and Fourier transform infrared spectra. The effects of the resin viscosity, emulsifier, nucleating agent, curing agent, silicone oil, microwave heating time and blowing agent on the structure of foam were investigated. Results showed that the properties of foam were decided by not only the molecular structure but also structure of foam, and the carboxylated Fe₃O₄ nanoparticles can improve the toughness and flame retardant properties of magnetic foam obviously from both aspects. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2688–2697, 2013

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INTRODUCTION

As known to all, the melamine foam which has a three-dimensionally network structure is widely used in filtering liquid,¹ clean surface,² absorbing sound,³ insulating from heat and electricity, building components, aircraft insulation, packaging and sanitary ware.⁴ Because melamine riches in nitrogen and has a stable triazine ring structure, the melamine-formaldehyde foam usually advances in high stability and fire-retardant. In addition, the three-D crosslinked structure is easy to break and its products are fragile.⁵ According to the previous work, melamine resin generally was modified by the chemical and physical methods to improve the toughness.⁶

Melamine resin was modified through the following channels in traditional way: First, changing the melamine on the amino⁷; Second, adding a modifier during the resin synthesis process⁸ to cap on the activity of hydroxymethyl^{9,10}; Third, modifying by physical methods, including adding a flexible polymer or nanoparticles into precondensate.⁶ Basic purpose of those methods is to benefit the relative movement among the molecular chains. Further, the added nano-particles can play role as the nucleating agent, so that the foam is more fine and uniform.

Literature showed that the good dispersibility of nanoparticles in resin can improve the toughness of the plastic.¹¹ Fe₃O₄ particles have been extensively studied by many group.^{12–14} Metal-chelating agent may increase the dissolution of ironoxides.¹⁵ Furthermore, carbonyl iron particles are better chooses for foaming in acid environment. Melamine resin which contains a large number of the hydroxymethyl group, under certain conditions, may react with hydroxyl group on the surface of the carboxylated Fe₃O₄ nanoparticles. This will reduce the possibility of cracks in foam caused agglomeration.

In addition, the synthesized melamine foam will be magnetic. Magnetic polymeric composites have very broad application prospects in the fields of electronics industry, magnetic shielding materials,¹⁶ absorbing stealth materials,^{17,18} microbial culture,¹⁹ biomedical research,²⁰ scientific instrument and communication equipment. Besides, the magnetic foam can be used as carrier for the growth of bacteria and cell which can be effectively stimulated in the steady weak magnetic field. Magnetism is not only conducive to the proliferation and metabolism of the microorganism but also able to shorten its growth cycle, so that the biological activity of the microorganism and cells can be greatly improved.²¹ Magnetic effects can also greatly improve the efficiency of wastewater biodegradable.^{15,22} Low efficiency of

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biological sewage treatment facilities and large area conditions could be improved by magnetic foam. Generally, the magnetic foam widely used is mainly based on polystyrene²³ and polyurethane foams.²⁴ These foams possess excellent insulating and mechanical properties, but their heat distortion point are low (particularly below 100°C), so the use of magnetic foam was limited. Moreover, this magnetic foam is also highly flammable and releases a noxious vapor when burning. One solution to solve the above problems is to add halogen-containing or phosphorus-containing flame proofing agents, but this is not an ideal approach because it affects the processing characteristics adversely, and it leads to the formation of hydrogen halides. In addition, the magnetic foams were observed to have slightly worse thermal stability in air than pure PU foams.²⁴

In principle, melamine-formaldehyde foam with magnetic will overcome some of the deficiencies of the existing magnetic foam to meet practical needs better. The magnetism of foam is determined by the magnetic particles embedded in resins.^{25–27} Magnetic particles are usually made by inorganic salts of Fe, Au, Ag, Bi, and so forth.^{28,29}

In this work, to increase the flexibility of foam in molecular structure, two kinds of new resins named melamine-ethanolamine-formaldehyde (MEF) and melamine-glycol-formaldehyde (MGF) were synthesized. The chain lengths between the triazine rings in the MEF and MGF have been increased. A novel melamine-formaldehyde-Fe₃O₄ foam was obtained by using MEF resin, MGF resin and nano-Fe₃O₄ as major materials. The foam structure comprises a plurality of mutually connected three-dimensionally branched webs. The length-diameter ratio of the foam reaches up to 15 : 1. The article is arranged as follows. In the experimental section, the synthesis of nano-Fe₃O₄, MEF, MGF resins and the process of producing foam are described in detail. The two resins and the foam were characterized by means of ¹³C-NMR, SEM, UTM, LOI, TG-DTA, and FTIR. In the section of results and discussion, the physical structure of foam was investigated by considering a series of factors referring to curing agent, emulsifier, nucleating agent, foaming stabilizer and resin's viscosity. Conclusions were listed at the end of the article.

EXPERIMENTAL

Materials

NIAX Silicone L-580 was purchased from Momentive Performance Materials Inc. All other chemicals including melamine, formalin, ethanolamine, phenol, pentane, glycol, Sodium oleate Alkylphenol polyoxyethylene(10)ether (OP-10), FeCl₃·6H₂O, FeSO₄·7H₂O, NH₃·H₂O, HCl, and Ethylenediaminetetraacetic acid disodium salt (EDTA) were bought from Tianjin Guangfu fine chemical research institute and were of analytical grade. All those reagents were used without further purification.

Synthesis of Fe₃O₄ Nanoparticles

Fe₃O₄ nanoparticles were synthesized by the coprecipitation. 1.1 g of EDTA and 10 mL of ammonia (28%) were added into a 100 mL aqueous solution which contain 2.9 g of FeCl₃·6H₂O and 1.5 g of FeSO₄·7H₂O, followed by stirring at 80°C for 1 h.

Then, the solvent was evaporated and concentrated to 30 mL. The leaves are fairly stable.

Synthesis of MEF

100 g formalin (contained formaldehyde 37%) and 5 g ethanolamine were put into a four-necked flask. The mixture was refluxed, stirred and thermostatic in an oil bath at 90°C. When the temperature reached 90°C, 50 g melamine was added into the flask. After the solution became clear, 5 g phenol was added. 30 min later, the solution was cooled quickly to below 60°C in ice-water bath. The water was removed by vacuum distillation, until the solid content reached 70%. The mixture was cooled to room temperature in ice water bath and resin MEF was obtained.

Synthesis of MGF

18 g paraformaldehyde, 37.2 g glycol and 12 g melamine were put into a flask respectively, and five drops of 30% sodium hydroxide solution in the flask. The aqueous solution was kept at 75°C in oil bath. After becoming clear, the temperature of mixture was decreased to 55°C in ice bath and the pH was adjusted by adding five drops of 98% sulfuric acid. Then solution was incubated at 55°C for 1 h and the resin MGF was obtained. Stir was carried out during the whole process.

Foaming

Resins MEF and MGF (totally 30 g), OP-10 (from 0.6 to 2.4 g), silicone L-580 (0.6 g), pentane (1.5 g), formic acid (88%, 3 g), melamine powder (2 g) and Fe₃O₄ solution (0.5 g) were mixed in a 1000 mL beaker and stirred slowly. The mixture was foamed for 30–60 s in a Galanz microwave oven (model P80D23N1L-A9(S0)) at 800 W/2450 MHz. The uncured melamine-formaldehyde-Fe₃O₄ foam was obtained which was soft in silver-gray color.

Hot-Cure

The foam was treated in a hot air blast oven at the temperature of 220–250°C for 1 h. The target melamine-formaldehyde-Fe₃O₄ was obtained

Characterization

The cross polarization magic angle spinning (CPMAS) ¹³C-NMR spectroscopy for resin MEF and MGF were carried out by using a Bruker AvanceII 400 spectrometer with a Bruker 4 mm double resonance probe-head operating at 100.62 MHz for ¹³C operating at a spinning rate of 6 kHz. Field-emission scanning electron microscopy (FE-SEM) image of the foam was obtained with a FEI Quanta 200 scanning electron microscope. The samples were sputter-coated with gold. Limiting oxygen index (LOI) experiments were performed on a HC-2 limiting oxygen index tester. Material Mechanical Performance was performed on Electronic Universal Testing Machines. Thermogravimetry measurement (TG) was conducted on a Diamond TG/DTA thermal analyzer at a heating rate of 20°C min⁻¹. The measurements were taken from room temperature to 715°C under nitrogen flow. Calculation of the average pore size by counting the number of pore both in parallel and perpendicular direction of foamed in 5 cm, and then 10 cm divided by the total number of pore. Fourier transform infrared (FTIR) spectra were collected on a Nicolet Avatar 370 infrared spectrometer using

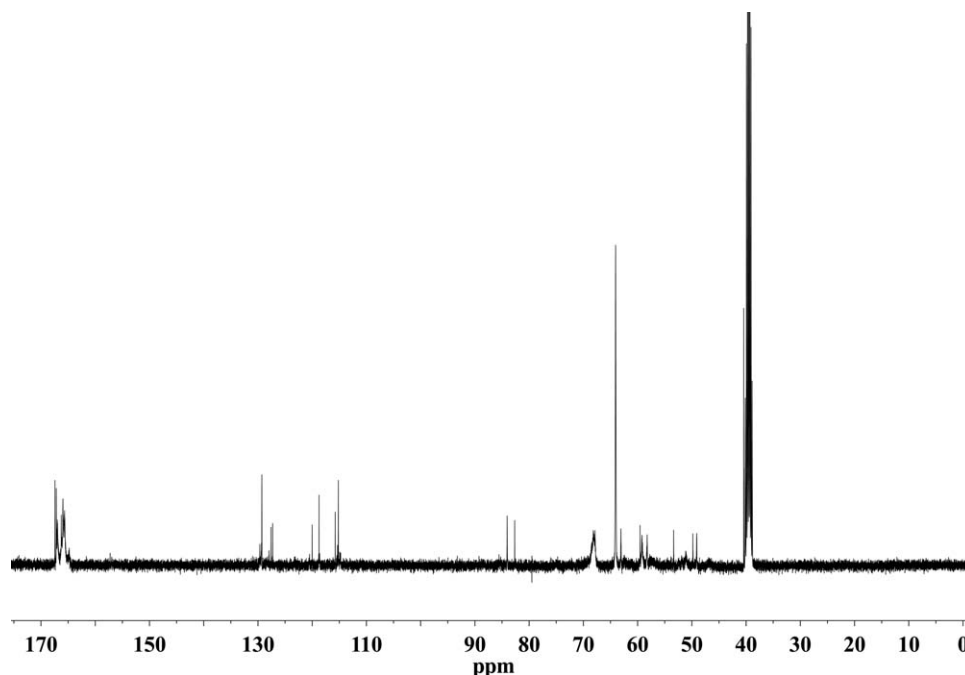


Figure 1. ^{13}C -NMR spectra of MEF. MEF had been dried at 120°C for 10 h before characterization. The dry resin was grind before dissolved in $\text{DMSO-}d_6$.

pressed KBr discs. The FTIR spectrum was recorded with a resolution of 1 cm^{-1} over the range of $4000\text{--}400\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Preparation of Fe_3O_4 Nanoparticles

Dispersibility of nanoparticles is a problem due to surface effect, Van der Waals' force, the Coulomb force and the magnetic force of Fe_3O_4 . Agglomeration of the nanoparticles will not only affect the magnetic properties, but also seriously affect the toughness of the foam. On the contrary, nanoparticles with good dispersibility will be conducive to improve the toughness of the plastic. Moreover, nanoparticles have stability under the weak acid condition, because the foaming must be processed under a weak acidic condition. As mentioned earlier, the Fe_3O_4 nanoparticles were obtained by a traditional coprecipitation. Carbonyl iron particles which were made in this way are chosen because of the high permeability, low remanent magnetization, and high saturation magnetization which can fulfil the above two conditions mentioned above. The surface of nanoparticle is full of carboxyl, so it could be easily dispersed in the resin. The surface of different morphologies of the Fe_3O_4 also can be treated after nanoparticles were synthesized.³⁰ In this work, the Fe_3O_4 drying, for reasons of the impurities are NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$, both of them are conducive to curing.³¹ Thus, the hard agglomeration in drying process could be avoided. In the Fe_3O_4 FTIR spectrum, the strong peak at 1627.9 and 3431.7 cm^{-1} can be assigned to $\text{C}=\text{O}$ and $-\text{OH}$, respectively. The nanoparticles dispersed in the water were stable and no precipitate was produced in 1 week.

Synthesis of MEF

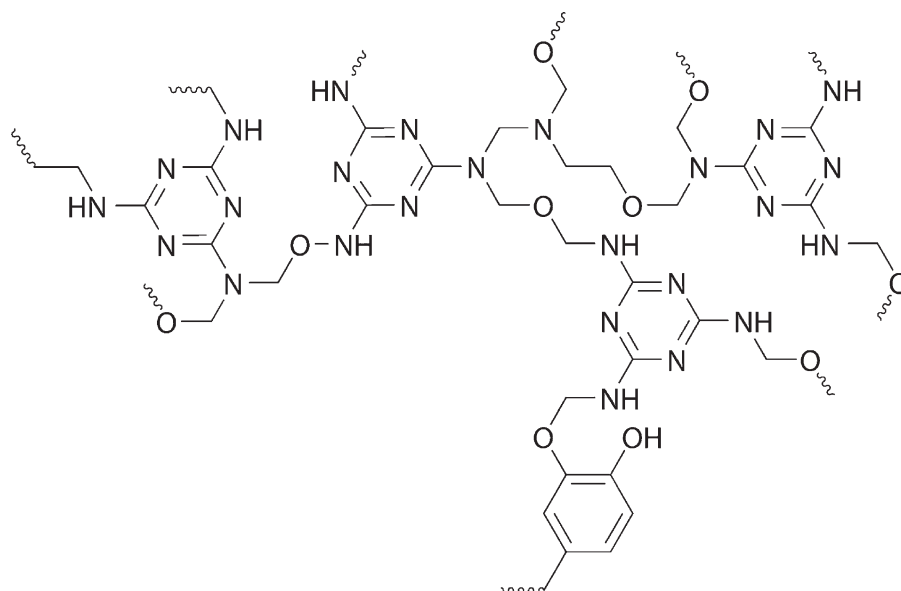
In the synthesis of MEF resin, ethanolamine was chosen to provide alkalescency. Moreover, it can increase the length of chain

between two triazine rings to benefit the flexibility of the foam. However, when the weight of ethanolamine was added more than 10% of melamine, it would cause curing difficulties. The ^{13}C -NMR measurements for resin MEF were shown in Figure 1. The peak at 39.5 ppm represents chemical shift of the solvent $\text{DMSO-}d_6$; the peaks shown from 165 to 168 ppm represent the C atoms in triazine rings; the peaks from 115 to 130 ppm are assigned to C atoms in phenolic; ^{13}C -NMR (100 MHz, $\text{DMSO-}d_6$, δ : ppm): 64.05 (NHCH_2OH), 68.10 ($\text{CH}_2\text{NCH}_2\text{N}$), 68.17 ($\text{NHCH}_2\text{OCH}_2\text{NH}$), 84.05 (HOCH_2OH), 84.60 ($\text{HOCH}_2\text{OCH}_2\text{OH}$), 49.84 ($\text{N}(\text{CH}_2)_2\text{CH}_2\text{CH}_2$), 59.52 ($\text{NCH}_2\text{CH}_2\text{OH}$). From the NMR data in Figure 1 and FTIR data in Supporting Information Figure S1, we can conclude the structure of resin MEF which was shown in Scheme 1.

Synthesis of MGF

Difference from the resin MEF, MGF was synthesized from paraformaldehyde, glycol and melamine. Traditionally, etherification between monohydric alcohol and melamine resin can make the resin more stable. Here, we introduced the glycol which is a dihydric alcohol as etherification agent in the experiment. On the one hand, the stability of the resin was improved at a certain degree. On the other hand, the excess introducing of the glycol the over etherification and increases the chain length between triazine rings so as to improve the flexibility of foam.

In the first stage of the synthesis, the pH was adjusted to alkaline which is conducive to the depolymerization of paraformaldehyde and the reaction between melamine and formaldehyde. It can also reduce the extent of reaction of the formaldehyde and the glycol. Furthermore, the pH and temperature are very important to the melamine resin in the second stage. If the pH value is too low, the hydroxyls in melamine resins can react



Scheme 1. Structure of MEF. Possible connection patterns are shown in form of ether and methylene linkages.

more easily with each other than those between melamine resin and glycol. Conversely, a pH value which is greater than 7 makes the etherification very slow. Similarly, a high temperature condition always makes the resin easily cured, and the reaction temperature is usually lower than 60°C.

In addition, the glycol can be introduced either in the synthesis of the resin or in the foaming process. The difference between the two methods was that the utilization of glycol before foaming process is quantitatively more effective than that in the foaming process. Because foaming process is completed within

a very short time and the glycol has an influence on foaming process. Under the same conditions, the pore size becomes larger after adding glycol. As shown in Figure 2, the chemical structure of the MGF was analyzed by ^{13}C -NMR. ^{13}C -NMR (100 MHz, $\text{DMSO-}d_6$, δ : ppm): 67.49 ($\text{OCH}_2\text{CH}_2\text{O}$), 69.37 ($\text{OCH}_2\text{CH}_2\text{OH}$) 61.11 ($\text{OCH}_2\text{CH}_2\text{OH}$). According to the NMR data, we concluded the structure of MGF which was shown in Scheme 2. Besides, in the FTIR spectra, the peaks at 2935.66 and 2873.94 cm^{-1} (Supporting Information Figure S2) are characteristic peaks of the methylene.

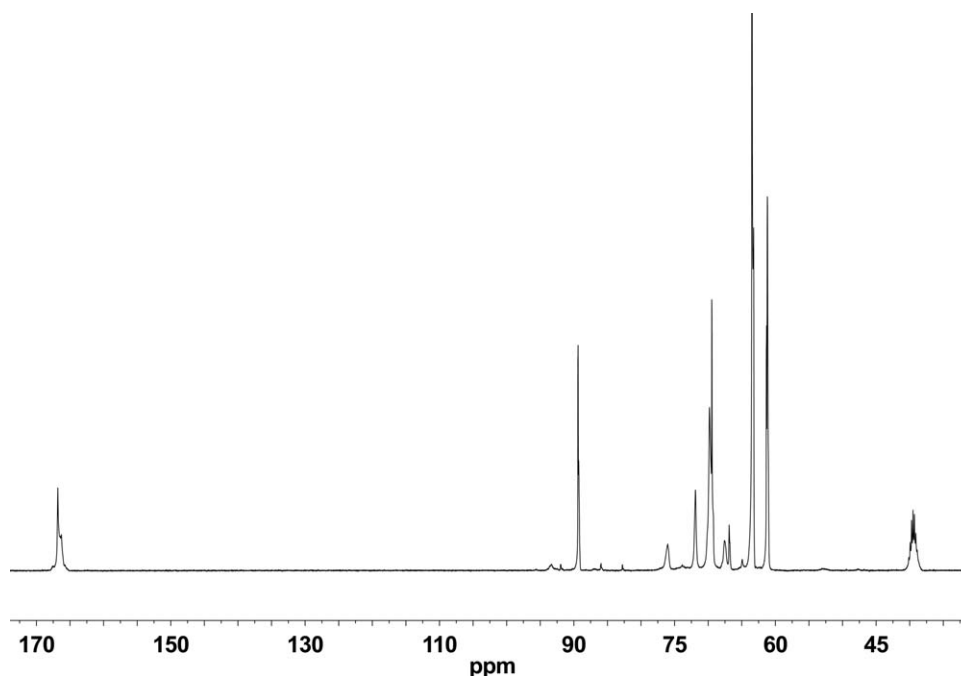
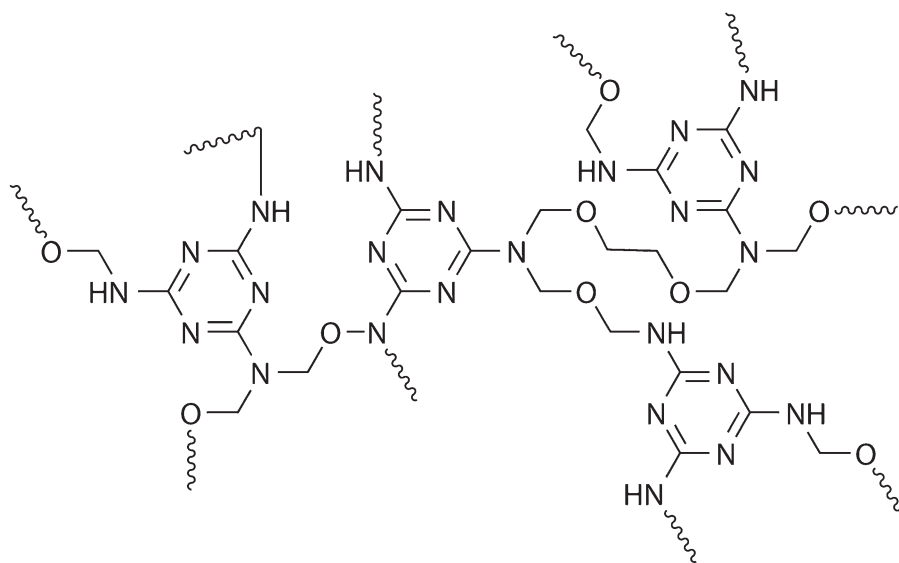


Figure 2. ^{13}C -NMR spectra of MGF. MGF was dissolved in $\text{DMSO-}d_6$ without further processing.



Scheme 2. Structure of MGF. Possible connection patterns are shown in form of ether and methylene linkages.

Structure Control Method

Structure is crucial to the properties of the foam. Structure of melamine foam can be affected by many factors such as curing agent, emulsifier, viscosity, stirred speed, microwave heating time, nucleating agent, and foaming agent. In the experiment, several foams were synthesized under different conditions, and corresponding microstructures were listed in Figure 3, the details of foam structure were shown in Supporting Information Figures S4 and S5. In the following, several factors such as (1) curing agent, (2) viscosity, (3) emulsifier, (4) microwave heating time, and (5) foaming agent were investigated for the microstructure of the foam and foaming process. To study the influence of various factors on the structure, the formula used resin 30.0 g, emulsifier OP-10 1.5 g, and 3.0 g blowing agent pentane, formic acid 3.0 g as a curing agent, 0.6 g silicone oil, and microwave heating time is 45 s except variables.

Curing Agent

The effect of the curing agent on the foam was mainly reflected on the curing speed. Generally speaking, only when the foaming speed matches the curing speed can a nice structure of foam be obtained. If curing speed was faster than the foaming speed, both the opening ratio and length–diameter ratio would be decreased. Conversely, the foam would be collapsed. Furthermore, the dosage of the curing agent was important for the foaming process. In addition, the curing agent is an acidic substance; it can destroy the hydrogen bonding in the resins to reduce the viscosity. In this experiment, 85% formic acid was used as curing agent to investigate the effect of the amount of formic acid on the structures of the foam. As shown in Figure 3, the amount of formic acid affected the structure significantly, over dosage of formic acid would decrease the opening rate [Figure 3(f)]; on the contrary, an insufficient use would make the foam has a larger length–diameter ratio [Figure 3(e)]. The optimal dosage for formic acid was 5–15%. If curing agent is out of range, curing or foaming difficulties will appear. The dosage of curing agent affected

significantly the length–diameter ratio of the foam. However, the pore size in the foam had been less affected by the consumption of curing agent. In this work ethanolamine which was used as flexibilizer can decrease the acidity of curing agent by forming a buffer solution. In the curing process, the release of hydrogen ions can keep the curing process smooth in some degree. Because of the formation of the buffer solution, the pH value varied a little, the kind of the curing agent affected on the pore size of foam is not apparent.

Viscosity

Viscosity is another important factor for the structure of foam. The average pore size in the foam becomes smaller as the viscosity increasing. If the viscosity of resin is too low, it will increase the pore size and unevenness appeared. However, when the viscosity is more than 6000 mps, it makes the foaming difficultly so as to result in the bubble uneven and the length–diameter ratio low. Viscosity of the resin is decided by the degree of polymerization and the solid content. Here, we divided it into two sections for discussion.

Degree of Polymerization of the MEF. The greater degree of polymerization is, the smaller pore size of the foam becomes. That is because polymerization degree affects the curing time. When degree of polymerization is too low, the curing will needs a long time. Generally speaking, the degree of polymerization is decided by the temperature and the time of heating in process of synthesis of MEF. To study the relationship between the pore size and degree of polymerization, we have investigated the pore size at different heating times (0–120 min) and temperatures (80–90°C). As shown in Figure 4, when the temperature is 80°C (see curve a), if the heating time is more than 120 min, the viscosity of resin will be too high to foaming; If the heating time is less than 1 h, the production will be uneven. Similarly the curve b and c show the relationship between the pore size and heating time at the 85 and 90°C. Heating time should be controlled in a certain scope, to avoid viscosity of resin too high to prepare foam.

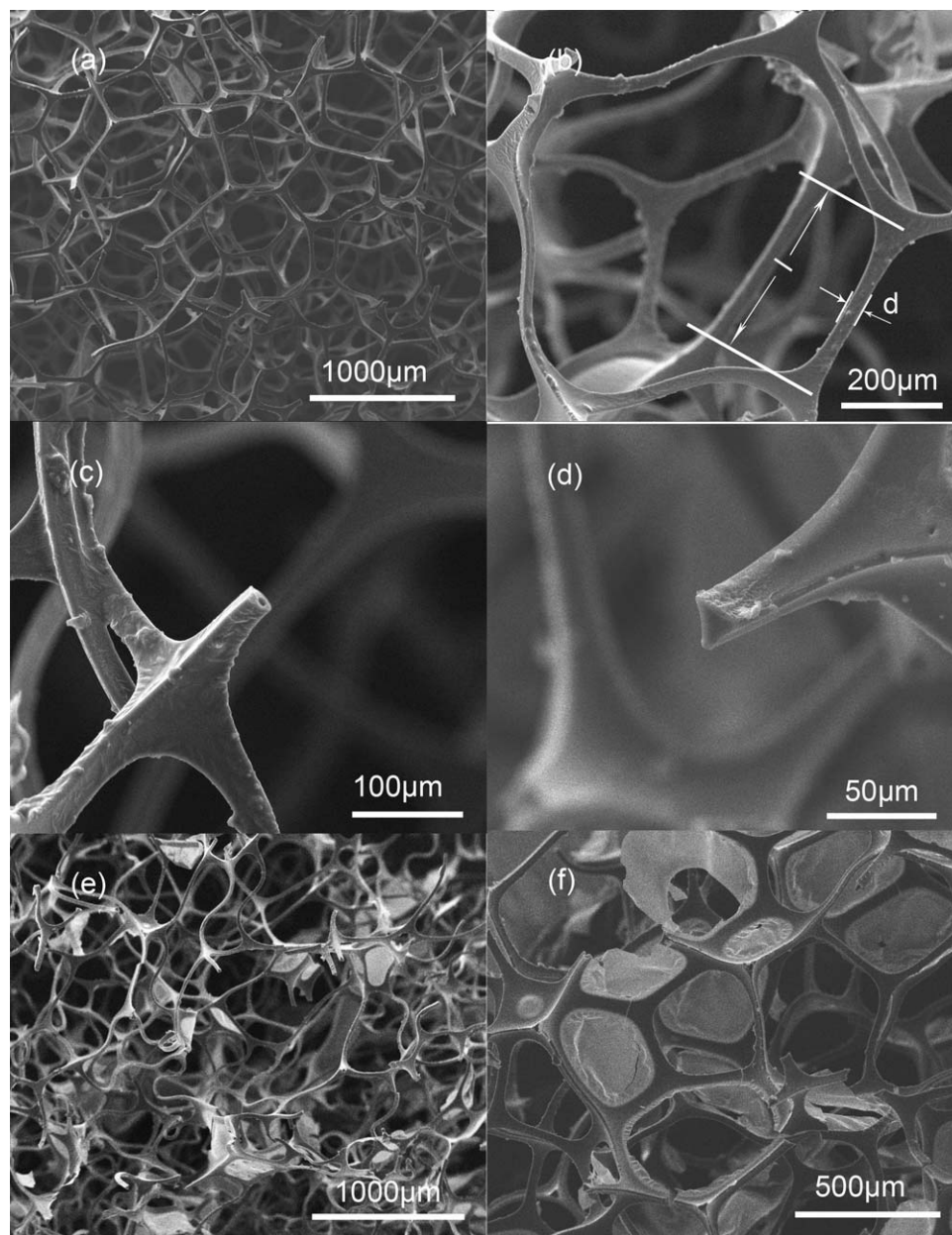


Figure 3. SEM micrographs of melamine foams. (a) Prepared under optimum condition. (b) A multiple ring in the foam. (c) Cross-section of fiber in the foam whose solid content of resin was less than 70%. (d) Cross-section of fiber whose solid content of resin was more than 70%. (e) The foam structure whose curing speed is slower than foaming speed. (f) The foam structure whose curing speed is faster than foaming speed.

Solid Content. Besides, the increase of the water content can reduce the amount of the foaming agent, nevertheless, the excessive moisture will reduce the density of the curing resin and it is easy to form a hollow structure in the inner of the webs. From Figure 3 and Supporting Information Figure S7, we can find that the curing resin is hollow. Those hollow structures make the foam fragile. In order to avoid this phenomenon, the water content must be reduced.²⁶ Solid content not only related to water content but also to the degree of reactivity. The free formaldehyde is reduced as the reaction proceeds. In the experiment, we found the optimum of the solid content is 70%. When the solids content is more than 70% the hollow in resin

will disappear [see Figure 3(d) and Supporting Information Figure S8].

Microwave Heating Time

In this work, the foam was prepared by microwave blowing method. Microwave heating time is investigated to attain the best condition. Figure 5 lists the relation between time and pore size. Results showed that the heating time affected the pore size obviously. When the heat time is less than 30 s, the foam is difficult to cure. With the heating time increasing from 30 to 75 s, corresponding pore size of the foam also increases gradually from 150 to 800 μm . However, a too long heat time will cause

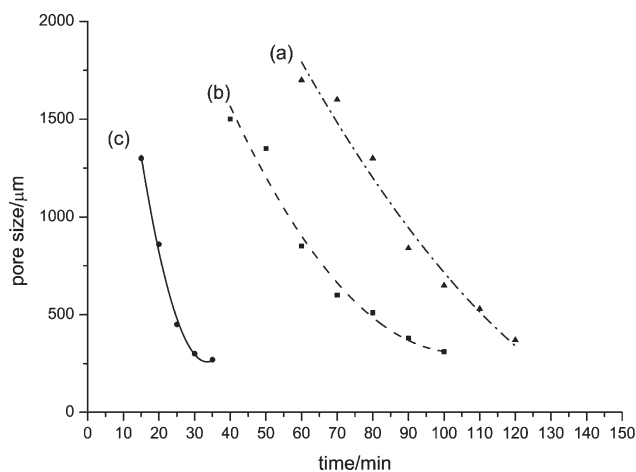


Figure 4. The relationship between the average pore size of resin MEF and heating time at different temperatures. (a) 80°C, (b) 85°C, (c) 90°C.

the web of foam hollow. After 1 min the pore size almost changes a little, because the curing process finished.

Emulsifier

Emulsifier plays an important role in decreasing the surface tension. Only the suitable surface tension can make the foaming successful. Emulsifier can form the micelles and latex particles which can be used as nucleating agent¹⁶ to make the foam uniform, fine and smooth. Too much emulsifier leads to the difficulty of curing. Figure 6 shows the relationship between the pore size and emulsifier. As the emulsifier increasing, the pore size decreases significantly until the utilization of the emulsifier is 8% of the resin mass. However, when the amount of the emulsifier is over 8%, foaming is disadvantageous.

Blowing Agent

A blowing agent is a substance which is capable of producing a cellular structure via a foaming process. Nevertheless, the apparent density of the foam is controlled by the amount of the foaming agent. In experiments, we investigated several blowing agents in the foaming. Results showed that if diethyl ether,

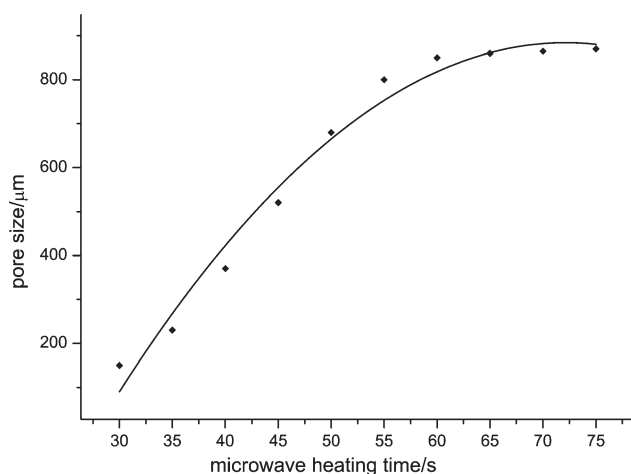


Figure 5. The relationship between pore size and microwave heating time. 30 g resin was continuous coverage in the 1024 MHz frequency band at 800 watts of power.

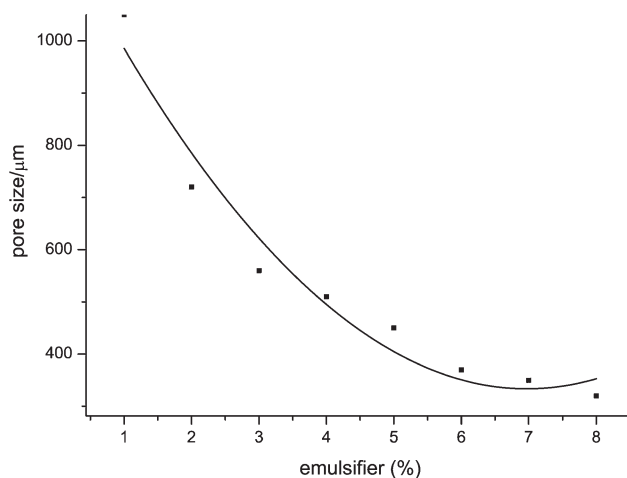


Figure 6. The relationship between foam pore size and emulsifier.

methylene chloride and acetone were used as blowing agent, the foam usually had very wide pore size distributions. Nevertheless, N-hexane and cyclohexane were used as blowing agent, the average pore size can reach 3 mm and the foam had very narrow pore size distributions. Different foaming agents have different boiling points. Different viscosity of the resin at the boiling point of a blowing agent leads to different pores. Besides, the pore distribution is also determined by the dispersion of blowing agent in the resin. The uniformity of dispersion directly affects the uniformity of the foam. The dispersion of blowing agent has a direct relationship with the emulsifier. In this work, the OP-10 was used as emulsifier, hydrophilic group polyethoxy ether disperses in resin, and the hydrophobic group is alkyl group. Further, based on the principle of the dissolution in the similar material structure, the better blowing agent is the one whose polarity is similar to the alkyl group.

Nucleating Agent

Nucleating agent is usually added to increase the amount of bubble. Objectively speaking, the nucleating agents are solid particles and most of them are nanoparticles. As toughening agent and nucleating agent, nanoparticles in the resin have been extensively reported in literatures.^{32,33} In this work, nano-silica, nano-titanium dioxide, nano-Fe₃O₄ were added to the resin respectively to investigate the toughness and nucleation performance of the foam. When nano-silica, nano-titanium dioxides were added more than 0.02% of resin, the foam became brittle. However, the foam will not tend to be brittle until nano-Fe₃O₄ is added more than 1%. Besides, nanoparticles can be added by two ways, one is before foaming; another is dispersing it in the solution of formaldehyde before the synthesis of resin. Both can make the foam more uniform and reduce the anisotropy. The former gives smaller apparent density and higher pore density of the foam than the latter, but the foam becomes more fragile than the latter. The reason may be that the air was taken into the resin when adding the nanoparticles. As is known to all, the air dispersed in the resin can be regarded as a foam nucleating agent. As a nucleating agent, the nanoparticles increase the number of the nucleating, but they are difficult to disperse in resin so that the foam tends to be fragile.

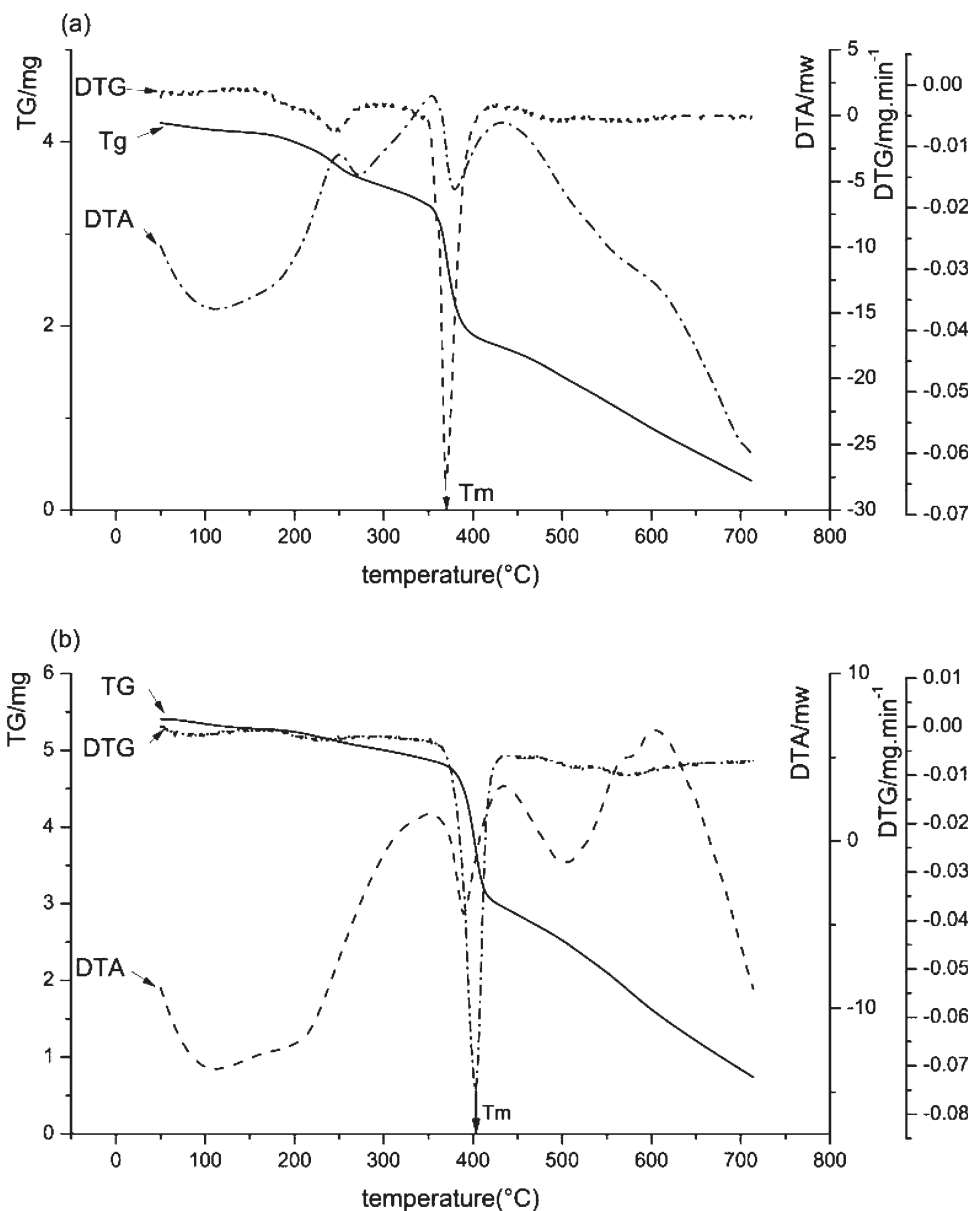


Figure 7. Thermo-Gravimetric/Differential Thermal of foams. (a) unripened melamine formaldehyde foam, (b) melamine-formaldehyde-Fe₃O₄ foam.

Conversely, melamine powder was also investigated as nucleating agent by adding before foaming. Powder can also put air into resin. Different with the inorganic nanoparticles, melamine powder react with resin without reunite each other and have a little impact on the chemical structure of the foam. Furthermore, it can be added as much as 10% of resin. In addition, the rapid agitation also benefits air to be dispersed in the resin. However, if the mechanical stir is too fast, the formation of latex particles will be destroyed, which is not conducive to the formation of micelles and emulsion. On the contrary, uniform latex particles may form a stable emulsion by a suitable stirring.

As known to all, the paramagnetic nano-particles can convert the electromagnetic energy into heat, this may make the nano-Fe₃O₄ as a heating point in mixture and as the nucleation sites of bubble.

Foam Stabilizer

Generally speaking, foam stabilizer has an important impact on both the bubble generation and the cell window stabilization stage. Suitable surfactants can give higher film elasticity, yield slower drainage rate and better foam cell stability.³³

In this work, the alcohols and silicone oil were used as the foam stabilizer. In our experiments, we found that the foam's apparent density is always more than 50 kg m⁻³ without foam stabilizer and easily form big holes inside of it. When emulsifier is ionic surfactant (SDS) and the alcohols (lauryl alcohol) was added as a foam stabilizer, the average pore size is small, but the bubble distribution is not uniform, some pore sizes are significantly larger than the average. Nevertheless, a good structure of foam was obtained by adding the silicone oil as stabilizer and OP-10 as emulsifier. The apparent density can be less than 3 kg

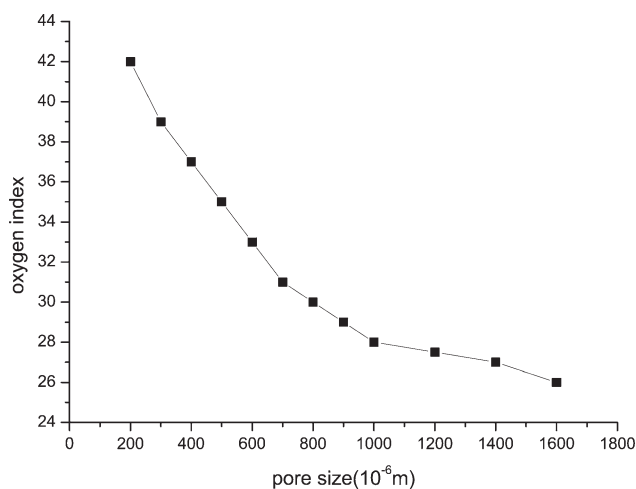


Figure 8. The relationship between pore size and oxygen index.

m^{-3} . Figure 3(a,b) shows the three-dimensional network structure of the foam by using the silicone oil in the foaming. Figure 3(b) is a part of the 3a at a high scope. It was observed that the net structure is combined by many five-membered rings, six-membered rings and a few four-membered rings. The webs mean length: width ratio is greater than 15 : 1. As shown in Figure 3(a,b), an ideal structure of the foam can be obtained by adding the silicone oil rather than alcohols. Because the emulsifier (OP-10) is nonionic, the foam stabilizer (silicone oil) is also nonionic. When the ionic surface active agent is mixed with a nonionic surfactant, nonionic molecules will be fitted into ion-molecule micelles, so the silicone oil cannot form an elastic film and lose the ability to stabilize foam.

Performance of the Foam

Figure 7 shows TG-DTA of the foam: 3a is the foam without adding the Fe_3O_4 or curing. 3b is the one with the Fe_3O_4 after hot-cure. Results showed that the major weight loss temperature range improved from 370.5 to 402.3°C after adding the Fe_3O_4 . A decalescence peak and loss of weight are near 250°C in Figure 7(a), the reason may be that a part of the ether bond in the foam is converted into methylene and methanol or formaldehyde releasing. Hence, the temperature of hot-cure should be close to 250°C. The decalescence peak at 503°C and exothermic peak at 602°C are due to the decomposition of the carboxyl group in nanoparticles. The peak at 434°C is an exothermic peak [Figure 7(b)] which proves that the resin had reacted with the Fe_3O_4 . To some extent, the reaction between the nanoparticles and resin can avoid the formation of defects because of the agglomeration of the nanoparticles.

The oxygen index is related to the apparent density, the pore density of the foam and the carbon content of the foam. The test method is in accordance with ISO4589-2. We found that the lower apparent density of the foam is, the lower oxygen index of the foam will be. When the apparent density of foam was lower than 5 kg m^{-3} , the oxygen index was lower than 28; when it is more than 10 kg m^{-3} , corresponding oxygen index will be higher than 35. And experiments showed that the larger the pore density of the foam, the better the flame retardant

properties. Nano- Fe_3O_4 improves the flame resistance of the material. Figure 8 shows the relationship between pore size and oxygen index. From the figure we find that the curve is not a line, this may be caused by the amount of emulsifier, the pore size is controlled by the dosage of emulsifier and it affects the carbon content of the foam.

It was found by tensile test and compression test that the pore size of the foam larger, the elongation at breaks bigger, but the smaller the tensile strength. Foam elongation at break is over 30% when the pore diameter is greater than 1.5 mm. The resin MGF increases the toughness and elongation at break. However, when resin MGF is added more than 30% of resin MEF, it caused a curing difficulty and the flame retardant property was reduced.

CONCLUSIONS

Accord to the ^{13}C -NMR of the MEF and MGF resins respectively, we can infer that the length of the molecular chain was increased. Adding carboxylates Fe_3O_4 can improve the toughness and flame retardant properties and make foam possess magnetic properties. The physical structure has an obvious relationship with the property of foam. Results showed that: (1) within a given range the increasing of the resin polymerization degree, the amounts of emulsifier and nucleating agent can significantly reduce the average pore size; (2) The amounts and species of the curing agent and blowing agent can significantly affect morphology of the foam; (3) The addition of the silicone oil when OP-10 is applied as the emulsifier benefits the stabilization of foaming process to obtain uniform and low apparent density foam; (4) the dosage of foaming agent is proportion to apparent density; (5) Microwave heating time affects pore size and morphology of the foam; (6) Foam performance change is due to not only the physical blends of Fe_3O_4 , but also chemical reaction. This reduces the cracks in foam caused by agglomeration.

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REFERENCES

- Seoighe, C.; Naumann, J.; Shvets, I. V. *Surf. Sci.* **1999**, *440*, 116.
- dovorany, J. R.; Alexander, S. F. US Patent 2007/0224409 A1, **2007**.
- Jaouen, L.; Renault, A.; Deverge, M. *Appl Acoust.* **2008**, *69*, 1129.
- Kosaka, Y.; Hattori, G.; hattori, G. US Patent, 2002/0163105 A1, **2001**.
- Tomita, B.; Ono, H. *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 3205.
- Bal, A.; Acar, I.; Güçlü, G. *J. Appl. Polym. Sci.* **2012**, *125*, E85.

7. Weiser, J.; Reuther, W.; Fikentscher, R.; Fath, W.; Berbner, H.; Zettler, D, H.; Voelker, H. US Patent 5,322,915, **1994**.
8. Imashiro, Y.; Hasegawa, S.; Okutani, T. US Patent 5,436,278, **1995**.
9. Spencer, F. R.; Spencer, F. R. US Patent 3,093,600, **1963**.
10. Absi-Halabi, M.; Lahalih, S. M.; Al-Khaled, T. *J. Appl. Polym. Sci.* **1987**, *33*, 2975.
11. Lee, J.; Yee, A. F. *Polymer* **2001**, *42*, 589.
12. Liu, Z. L.; Wang, H. B.; Lu, Q. H.; Du, G. H.; L. Peng, Du, Y. Q.; Zhang, S. M.; Yao, K. L.; *J. Magn. Magn. Mater.* **2004**, *283*, 258.
13. Zhang, D. E.; Zhang, X. J.; Ni, X. M.; Song, J. M.; Zheng, H. G.; *Cryst. Growth Des.* **2007**, *7*, 2117.
14. Sun, S. H.; Zeng, H. *J. Am. Chem. Soc.* **2002**, *124*, 8204.
15. Wang, M. Q.; Wang, N.; Tang, H. Q.; Cao, M. J.; She, Y. B.; Zhu, L. H. *Catal. Sci. Technol.* **2012**, *2*, 187.
16. Che, R. C.; Peng, L. M.; Duan, X. F.; Chen, Q.; Liang, X. L. *Adv. Mater.* **2004**, *16*, 401.
17. Zhuo, R. F.; Feng, H. T.; Chen, J. T.; Yan, D.; Feng, J. J.; Li, H. J.; Geng, B. S.; Cheng, S.; Xu, X. Y.; Yan, P. X. *J. Phys. Chem. C* **2008**, *112*, 11767.
18. Ajayan, P. M.; Tour, J. M. *Nature*. **2007**, *447*, 1066.
19. Zhou, L. C.; Li, G. Y.; An, T. C.; Li, Y. F. *Res Chem. Intermed.* **2010**, *36*, 277.
20. Salgueirino-Maceira, V.; Correa-Duarte, M. A. *Adv. Mater.* **2007**, *19*, 4131.
21. Bekhite, M. M.; Figulla, H.; Sauer, H.; Wartenberg, M. *Int. J. Cardiol.* **2012**; doi:10.1016/j.ijcard.2012.02.020.
22. Filipič, J.; Kraigher, B.; Tepuš, B.; Kokol, V.; Mandic-Mulec, I. *Bioresour. Technol.* **2012**, *120*, 225.
23. Yan, D. X.; Ren, P. G.; Pang, H.; Fu, Q.; Yang, M. B.; Li, Z. M. *J. Mater. Chem.* **2012**, *22*, 18772.
24. Zhang, J. J.; Li, L.; Chen, G.; Wee, P. *Polym. Degrad. Stab.* **2009**, *94*, 246.
25. Wibmann, S.; Wurmb, V. V.; Litterst, F. J.; Dieckmann, R.; Becker, K. D. *J. Phys. Chem. Solids* **1998**, *59*, 321.
26. Gamaliy, E.; Štěpánková, H.; Englich, J.; Kohout, J.; Snezhko, A.; Novák, P.; Brabers, V. A. M. *J. Magn. Magn. Mater.* **2002**, *242*, 732.
27. Giardiello, M.; McDonald, T. O.; Martin, P.; Owen, A.; Rannard, S. P. *J. Mater. Chem.* **2012**, *22*, 24744.
28. Reddy, N.; Anjaneyulu, K.; P. Basak, Rao, N. M.; Sunkara; Manorama, V. *ChemPlusChem.* **2012**, *77*, 284.
29. Andrés-Vergés, M.; Morales, M. D. P.; Veintemillas-Verdaguer, S.; Javier Palomares, F.; Serna, C. J. *Chem. Mater.* **2012**, *24*, 319.
30. Zhang, X. D.; Macosko, C. W.; Davis, H. T.; Nkolov, A. D.; Wasan, D. T. *J. Colloid Interface Sci.* **1999**, *215*, 270.
31. Mahnke, H.; Woerner, F. P.; Weber, H.; Kreibiehl, G. US Patent 4,540,717, **1985**.
32. Andrews, E. H.; Bevan, L. *Polymer* **1972**, *13*, 337.
33. Lee, J. L.; Zeng, C.; Cao, X.; Han, X. M.; Shen, J.; Xu, G. J. *Compos. Sci. Technol.* **2005**, *65*, 2344.