Phenolic Foams Modified by Cardanol Through Bisphenol Modification

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ABSTRACT: In this study, cardanol, a natural phenol, has been applied to toughen phenolic foam by bisphenol modification. In order to verify the occurrence of Friedel–Craft alkylation between cardanol and phenol on the side chain, FTIR, and NMR had been used to characterize the bisphenol successfully. With the introduction of cardanol, the viscosity of prepolymers increased. The SEM results demonstrated that the some cells with increasingly large size existed, when the dosage of cardanol increased. With respect to the mechanical properties, phenolic foams modified by 10 wt % cardanol increased by 22% in flexural strength and 28% in bending modulus compared to pure phenolic foams, which indicates that the incorporation of cardanol does improve the toughness of phenolic foams. In addition, the effects of different dosage of cardanol on the apparent density and thermal stability of phenolic foams were investigated. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39942.

INTRODUCTION

Compared with polyurethane[1] foam and polystyrene[2] foam, phenolic foam (PF) has excellent fire properties, including low flammability, no dripping during combustion, and low smoke density and toxicity.[3–5] In building thermal insulation area, the application of polyurethane foams and polystyrene foams is a potential threat to public security for their flammability properties, so the phenolic foams attract increasing attention.

However, phenolic foam is brittle and powdering, which severely restricts its application. It is necessary to study the toughening methods of phenolic foams. Over the past decades, there are main three ways developed to toughen phenolic foams: chemical modification, inert fillers, and fiber reinforcement. The main toughening mechanism of chemical modification is to introduce flexible chains into the rigid backbone chains of phenolic resin to enhance its toughness.[6] Given this mechanism, cardanol is taken into consideration as a toughing agent.

The cashew nut shell liquid (CNSL[7,8]), a by-product in the cashew nut industry, is composed of four major components, namely cardanol, cardol, anacardic acid, and 2-mehtylcardol (Figure 1). It is acknowledged that the useful component of CNSL is cardanol, which can be achieved by easy thermal decarboxylation of anacardic acid and vacuum distillation of CNSL. Actually, most of commodity CNSL has been processed by thermal decarboxylation to increase the content of cardanol. Many studies about the application of CNSL in the form of brake linings, surface coatings, paints, and varnishes as well as in poly-

mer production have been done.[9,10] There is little literature about the application of cardanol in phenolic foams.

Cardanol has been found to contain four components differing in side chain unsaturation namely saturation, monoene, diene, and triene. Due to the presence of the long unsaturated chain, cardanol can react with phenol via Friedel–Craft alkylation (Figure 2). Because of the phenol nature, the reaction product can react with formaldehyde under basic conditions to form resol-type prepolymer.[11]

In our study, cardanol reacted with phenol catalyzed by concentrated sulfuric acid. The products were purified by petroleum extraction and the following boiling water distillation. The structure of bisphenol was characterized by ^{1}H nuclear magnetic resonance (^{1}H NMR) and Fourier transform infrared spectra (FTIR). A series of prepolymer with different loadings of cardanol were synthesized, and the viscosity of prepolymer was measured by rotary viscosimeter at 0.6 rpm. Finally, phenolic foams with increasing content of cardanol were prepared. The apparent density was measured. The thermal stability was evaluated by TGA. The microstructure of cells was observed by SEM. Moreover, the compressive properties and bending properties of phenolic foams were characterized.

EXPERIMENTAL

Materials

Phenol, paraformaldehyde, sodium hydroxide, hydrochloric acid, and cyclopentane (analytical grade) were purchased from
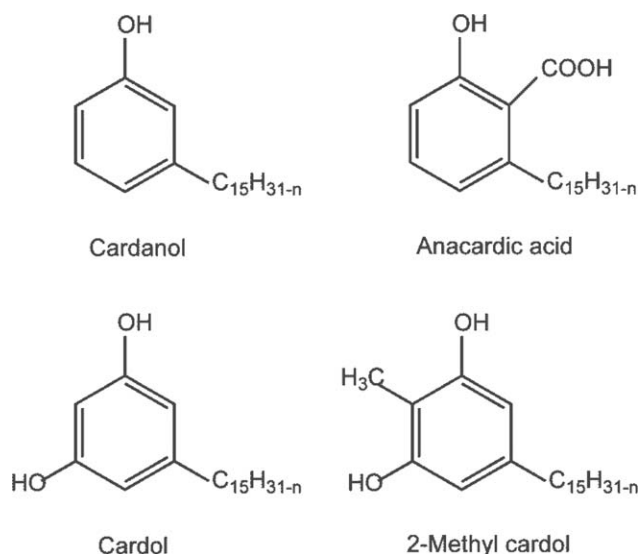
Figure 1. Natural compounds present in cashew nut shell liquid (CNSL).

Chengdu Kelong Chemical Regents Factory, China. Cardanol with purity up 99.00% was provided by Shanghai Wing Science and Technology Co., China.

Synthesis of Bisphenol
In the first step, a given amount of phenol and cardanol were added in a 250 mL, three necked, round-bottomed flask and heated to 100°C with rapid stirring, and then concentrated sulfuric acid was added into the flask. The reaction lasted for 3 h. According to the previous literature,[11] under this reaction condition, the conversion ratio of cardanol is up to 90%. The products were purified by petroleum ether extraction to remove the residual cardanol, followed by boiling water distillation to remove unreacted phenol before characterization.

In the second step, the mixture was cooled to 80°C and sodium hydroxide solution was added into the flask with stirring, and then paraformaldehyde was added in four times. This process lasted for 3.5 h and the resol-type prepolymer was obtained. Prepolymers with different content of cardanol were prepared in the same way. All the formulations were based on the following principles shown in Table I.

Preparation of the Samples of Phenolic Foam
A certain ratio of Twain-80 (emulsifying agent) and cyclopentane (foaming agent) were mixed in a 500 mL plastic beaker at room temperature, and then stirred with high-speed mechanical mixer for about 60 s. The mixture was mixed with hydrochloric acid (curing agent) and then stirred for 30 s. The obtained viscous mixture was poured into a foaming mould quickly, and cured at 70°C for about 20 min. The sample was cut precisely and used for the mechanical testing. The foaming formula was Twain-80 4 Phr, cyclopentane 10 Phr, and hydrochloric acid 10 Phr in weight to the weight of prepolymer.

Measurements and Characterization
Fourier Transform Infrared (FTIR) Spectra. Fourier transform infrared (FTIR) spectroscopy was obtained in the standard wavenumber range of 400–4000 cm^{-1} by Nicolet 6700 spectrometer (Nicolet Instrument Company) using KBr pellets.

^{1}H Nuclear Magnetic Resonance (NMR) Spectra. ^{1}H NMR spectra was recorded on an AVANCE 400 Bruker spectrometer at room temperature with chlorlform-d as the solvent.

Viscosity Measurement. Viscosity measurements were carried out with a NDJ-8S rotatory viscometer (Shanghai Jinhai Instrument Co., China) at 25 ± 0.1°C. The samples were measured at 0.6 rpm.

Thermogravimetric Analysis. TGA were carried out using a TA Instruments SDT Q600 at a heating rate of 20°C/min under a nitrogen flow from room temperature to 700°C. The weight of all samples was kept about 8 mg and heated from room temperature to 700°C.

Apparent Density. According to ISO 845:2006, the measurement of apparent density was performed. Samples were prepared in 50 mm square 5 mm thick. The result was calculated as follows:

$$\rho = \frac{m}{v} \times 10^6$$

where ρ is the apparent density (kg/m^3), m is the mass of sample (g), and v is the volume of the sample (mm^3).

Scanning Electron Microscopy (SEM). The microstructure of the phenolic foams was observed by an INSPECTF scanning electron microscope (FEI, Holand). Samples were carefully cut as slices from the freshly peeled surfaces.

Compressive and Bending Tests. Compressive and bending tests were performed by a AGS-J universal testing machine (Shimadu Co., Japan) in accordance with ISO 844:2004 and ISO 1209-2:2004, respectively. Five samples were carefully prepared and tested to obtain average values.

RESULTS AND DISCUSSION

Characterization of Bisphenol
The infrared spectra of the neat cardanol and the bisphenol are shown in Figure 3. The phenolic hydroxyl band is observed at
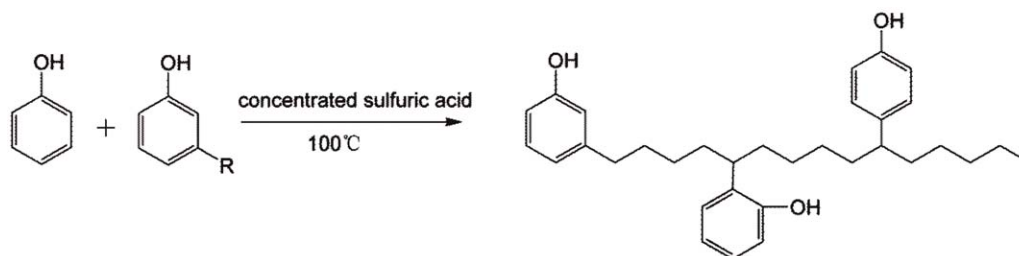

Figure 2. The synthesis route of bisphenol (R = $C_{15}H_{31-n}$).

Table I. The Principles Followed During the Synthesis of Prepolymers

	Principles
In the first step	The dosage of concentrated sulfuric acid is 1% of the mole of phenol.
In the second step	The total mole of phenols (phenol and cardanol)/the mole of formaldehyde=1 : 1.6.
	The mole of sodium hydroxide/the total mole of phenols=1 : 10.
	Actual concentration of the sodium hydroxide resolution is 20 wt % after reacting with the concentrated sulfuric acid.

3344.9 and 3345 cm^{-1} in the neat cardanol and bisphenol respectively. The –CH$_2$– peaks are found at about 2929 cm^{-1}, while the –CH$_3$ peaks are seen at 2854.4 cm^{-1} and are confirmed by the presence of their deformative peaks at 1347 and 1455 cm^{-1} in both infrared spectroscopies.

The vinyl vibrations at 994.7 and 722 cm^{-1} are corresponding to the side chain –C=C– bands in the neat cardanol. These peaks almost vanish in the spectra of bisphenol. Therefore, this indicates that the reaction between phenol and cardanol takes place on the –C=C– bands.

In the infrared spectrum of bisphenol, the peaks at 779.2 and 694 cm^{-1} attribute to the 1,3-substitution on the benzene, and the peaks at 827 and 752 cm^{-1} attribute to the 1,4-substitution and 1,2-substitution on the benzene, respectively. From the ^{1}H NMR spectrum of cardanol shown in Figure 4, the signal of double bond group protons is observed between 5 and 6 ppm in neat cardanol. In contrast, the signal of double bond group protons is not seen in the spectrum of bisphenol, which also indicates that the reaction has taken place on the double bond group.

The above results confirmed the structures of bisphenol as shown in Figure 2.

Viscosity

Figure 5 shows the relationship between the viscosity of prepolymer and content of cardanol measured at 0.6 rpm. With the dosage of cardanol increasing, the viscosity of prepolymer increases. The viscosity increases sharply when the addition of cardanol changes from 5 wt % to 10 wt %, while the increase of viscosity is not so noticeable when the dosage of cardanol changes from 10 wt % to 15wt %.

There are two main factors affecting the viscosity: molecular weight and molecular weight distribution. The relative molecular mass of cardanol is about 300, so the introduction of it increases the molecular weight of prepolymer, which contributes to the increase of viscosity. In contrast, the increase of content of components with low molecular weight will lead to decrease of viscosity. With the dosage of cardanol increases, the molecular weight of prepolymer increases, meanwhile the molecular weight distribution changes. There may still have another factor which affects the viscosity of the prepolymer. When the dosage of cardanol increases, increasing entanglement of the molecular

chains will increase the viscosity of prepolymer. The joint effect of those factors determines the changes of viscosity. That is why the increase degree difference said above happens.
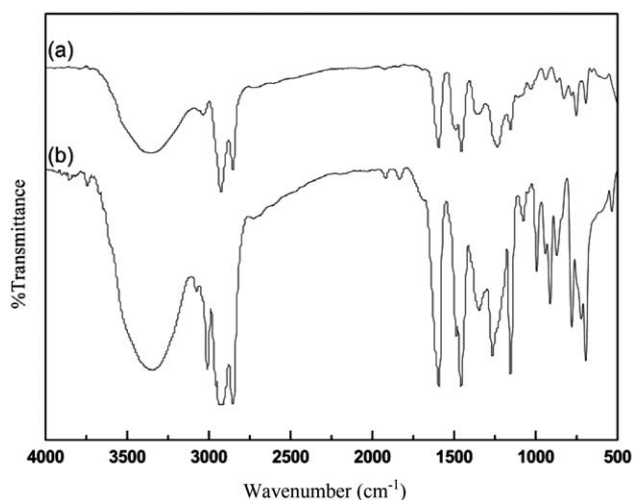
Apparent Density

The apparent density curves of phenolic foams modified by cardanol at different cardanol contents are shown in Figure 6. Compared with pure phenolic foams, the apparent density of modified phenolic foams reduces first and increases then with the increase of cardanol content. The apparent density of phenolic foam with 5 wt % cardanol had reached its lowest point, indicating that adding 5 wt % cardanol into phenolic foam can increase the expansion ratio. Compared with prepolymer with content of cardanol higher than 5 wt %, the prepolymer with the content of cardanol 5 wt % is not that sticky. The introduction of long side chains can improve the compatibility of prepolymer with foam agent. What is more, the molecules with long chains act as surfactants that can decrease the surface tension of prepolymer. Therefore, in the high-speed mixing process, it promotes the dispersion of foam agent in the prepolymer and is helpful to the formation of bubbles. Consequently, the bubbles grow uniformity at foaming temperature, resulting in the decrease of apparent density. But with the dosage of cardanol increasing from 5 wt %, the viscosity increases sharply, so that it becomes relatively difficult for bubbles to expand, thus the apparent density of phenolic foams increases.

Microstructure of Phenolic Foams

The microstructure of the phenolic foams is observed by SEM. The cell size and the effect of the addition of cardanol on the microstructure of phenolic foams are examined. As shown in Figure 7, the foams consist of a majority of closed cells. With the addition of cardanol, the cell size of phenolic foams decreases generally. However, with the increase of dosage of cardanol, large size cells exist.

When the content of cardanol is 5 wt %, a small number of large size cells exist with uniform distribution. Larger size cells exist in the foams with the dosage of cardanol 10 wt %. When the content of cardanol is up to 15 wt %, this phenomenon is most severe.

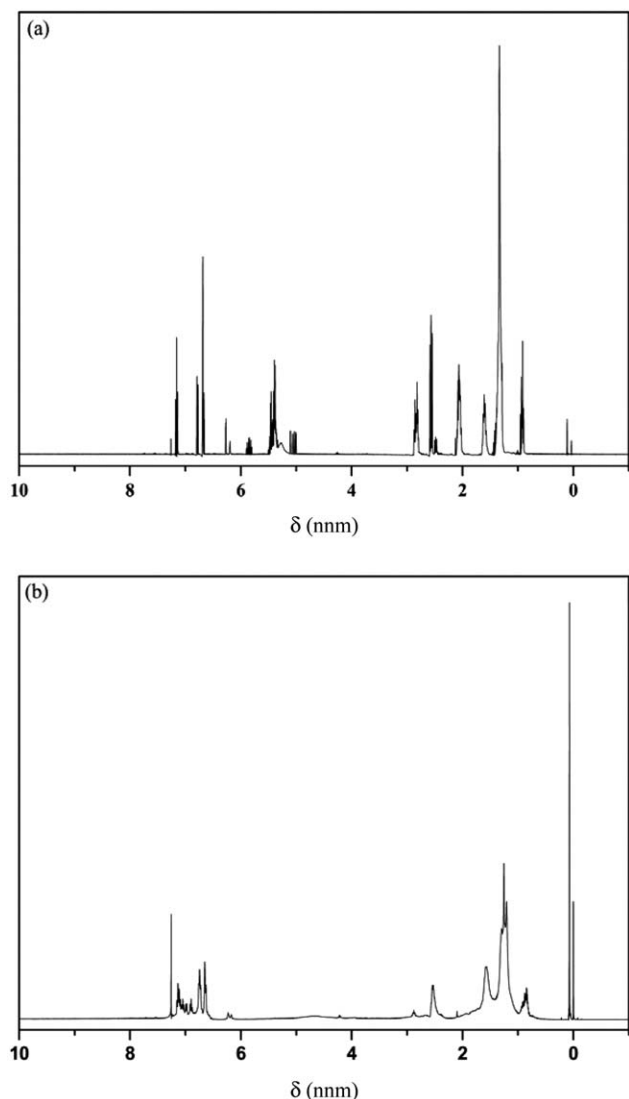**Figure 3.** Infrared spectra of (a) neat cardanol and (b) bisphenol.

Figure 5. Viscosity of prepolymer measured at 0.6 rpm with different contents of cardanol.

10 wt %, the compressive strength decreases slightly, but the modulus increases. The compressive performance deteriorates with the addition 15 wt %.

Figure 9 shows the relationship of flexural strength and bending modulus with the cardanol content, respectively. The flexural strength and bending modulus of modified phenolic foams increase, when the cardanol dosage is 5 or 10 wt %, and decrease with 15 wt % cardanol, compared to pure phenolic foams. Phenolic foams modified by 10 wt % cardanol increase by 22% in flexural strength and 28% in bending modulus, while the increase of bending properties with 5 wt % cardanol is slight. The bending results indicate that the introduction of cardanol improves the toughness of phenolic foams.

From the compressive and bending results, phenolic foams modified by 10 wt % cardanol have the maximal flexural strength and bending modulus with slightly lower compressive strength, compared to pure phenolic foams. The phenomenon that the compressive strength of modified foams with 10 wt %

Figure 4. NMR spectra of (a) cardanol and (b) bisphenol.

There are two factors leading to the existence of large cells. First, the increasing viscosity of prepolymer contributes a lot to the existence of cells with large size. High viscosity make the motion of molecule difficult, which means the decrease of cure rate and the imperfection of cure process, resulting in the combination of adjacent cells during the foaming process. Second, because of the steric hindrance, the difference of cure rate between molecules with long side chains and those without the side chains causes the difference in cell size too. Therefore, the results above demonstrate that with the increase of cardanol, the combination of cells in the cure process becomes increasingly obvious. Besides, when the dosage of cardanol is smaller than 10 wt %, cardanol has slight effect on the uniformity of cells.

Mechanical Performance

Figure 8 shows the curves of compressive strength and compressive modulus as a function of cardanol content, respectively. The addition of 5 wt % cardanol has no clear effect on the compressive properties. When the dosage of cardanol is up to
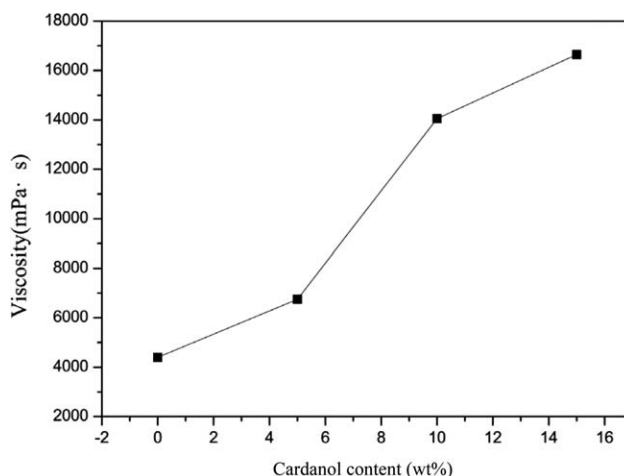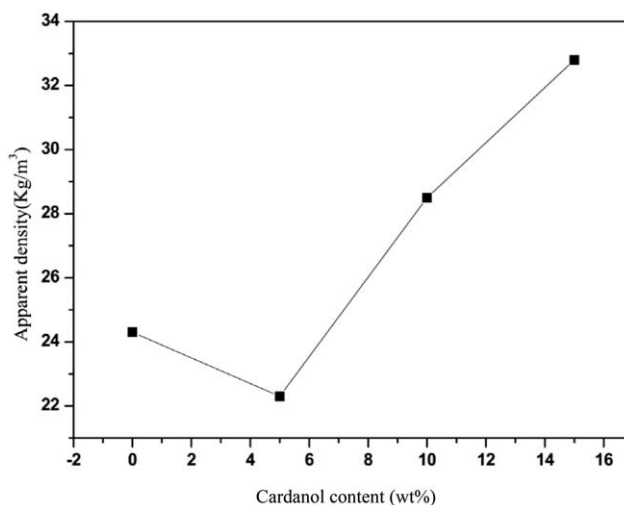

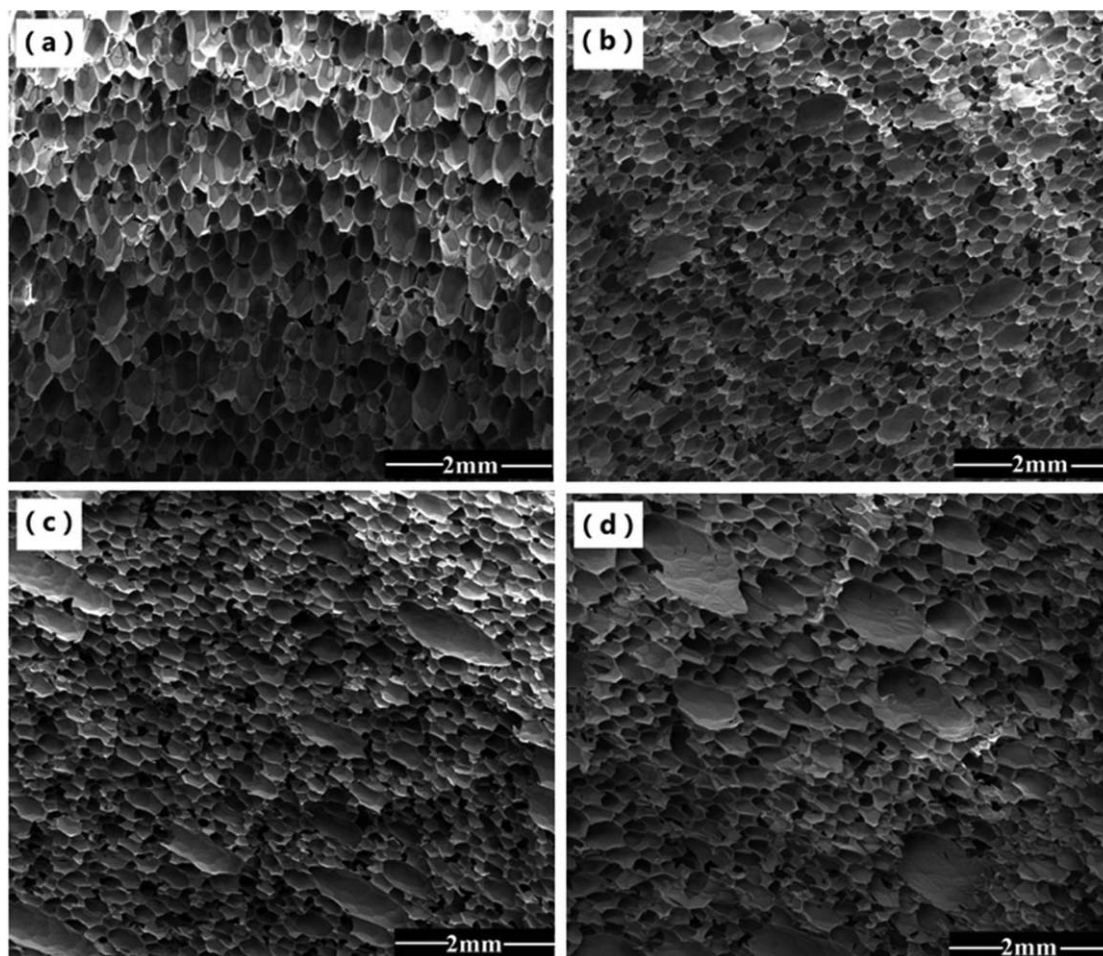**Figure 6.** Apparent density of phenolic foams at different cardanol contents.

Figure 7. SEM images (100×) of phenolic foams with different contents of cardanol (a: 0 wt %, b: 5 wt %, c: 10 wt %, d: 15 wt %).

cardanol decreases, but the modulus increases can attribute to the effect of deficiency and the increase of toughness, respectively. It seems that the effect of deficiency to the compressive properties is more obvious than that to the bending properties. The above results also indicate that when the dosage of cardanol is smaller than 10 wt %, the cure process and the cell structure are not affected obviously by cardanol. However, when the dosage of cardanol is up to 15 wt %, the mechanical performance of modified foams deteriorates, caused by the increase of deficiency in cell structure.
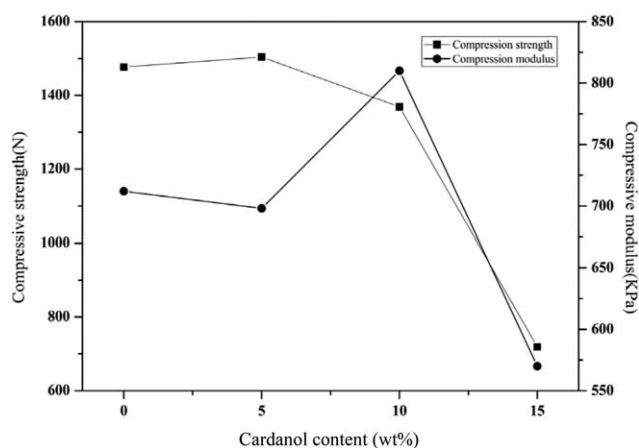

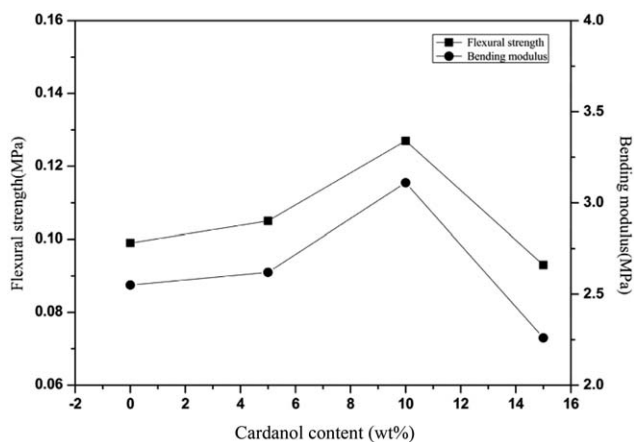**Figure 8.** Compressive properties of foams with different contents of cardanol.

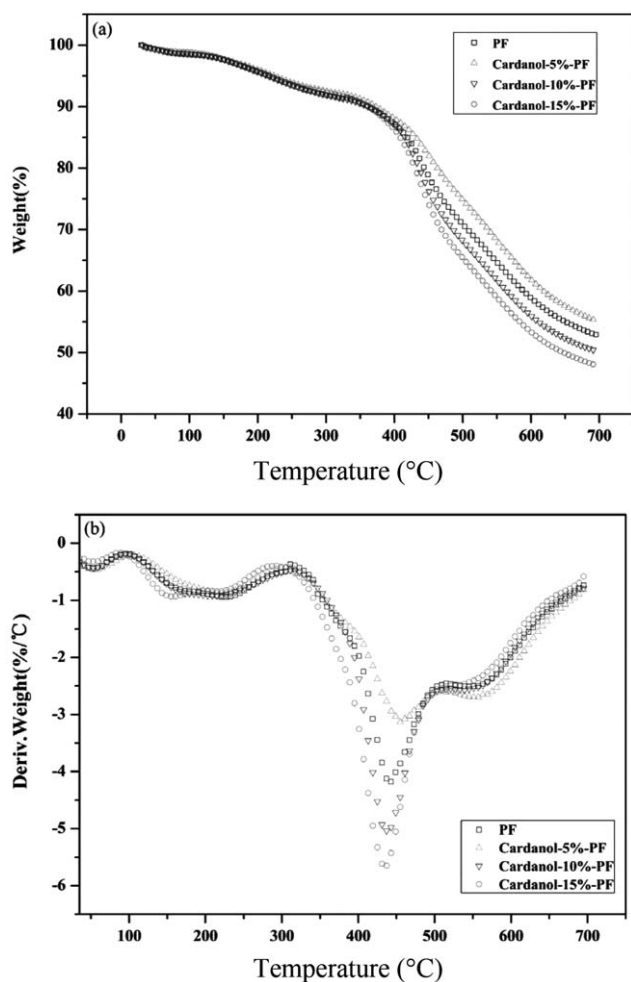**Figure 9.** Bending properties of foams with different contents of cardanol.

Figure 10. (a) TGA and (b) DTG curves of phenolic foams with different contents of cardanol at nitrogen atmosphere.

Thermal Stability

Figure 10 shows the TGA and DTG curves of phenolic foams with various content of cardanol. Table II records the mass residue of samples at 500 and 700°C.

Figure 10 demonstrates that the degradation process of phenolic foams is similar and the main degradation stage is between 300 and 500°C. Meanwhile, it is clearly seen that the initial decomposition temperature makes no difference and the main difference of the degradation process is the weight loss rate and mass residue.

From the DTG curve, the degradation rate of phenolic foams with 5 wt % cardanol is lower than that of other foams between

300 and 500°C and higher than that of other foams over 500°C, which is in accordance with the mass residue data shown in Table II. The char yield at 700°C for modified phenolic foams with 5 wt % cardanol is 1.5% higher than that of pure PF, while other modified foams obtain lower mass residue than pure PF. The results above indicate that the thermal stability of the structure as shown in Figure 11(a) is higher than that shown in Figure 11(b) and the addition of 5 wt % cardanol improves the thermal stability of phenolic foams.
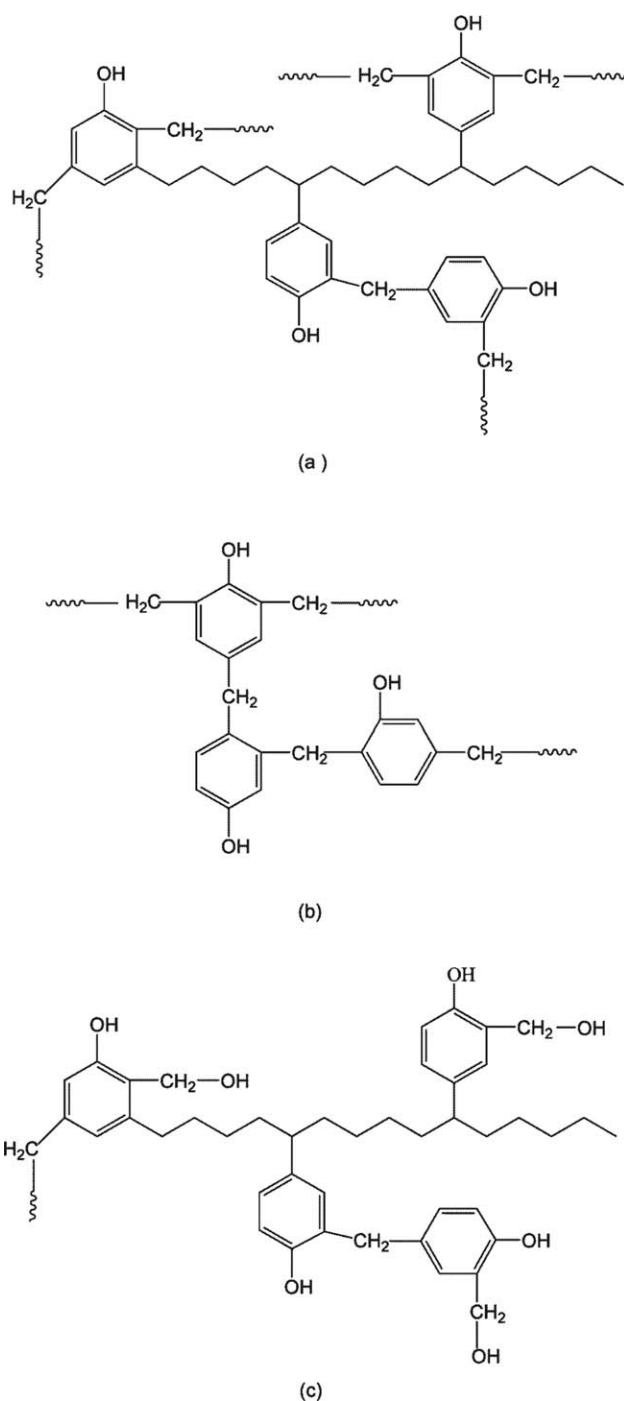
Figure 11. Three types of structures in phenolic foams.

Table II. TGA Data in Nitrogen of Pure PF and Cardanol–PF Systems

Sample no.	Mass residue at 500°C(%)	Mass residue at 700°C (%)
PF	70.87	52.72
Cardanol–5%-PF	74.82	54.21
Cardanol–10%-PF	68.12	51.54
Cardanol–15%-PF	64.88	47.62

Applied Polymer

When the dosage of cardanol is over 5 wt %, the high viscosity hinders the formation of the structure [Figure 11(a)] to some degree and increases the content of free hydroxymethyl group [Figure 11(c)], leading to the decrease of mass residue compared to the pure phenolic foams. Therefore, the thermal stability of foams decreases, which is obvious with the cardanol dosage 15 wt %.

CONCLUSIONS

In this study, we successfully synthesized phenolic foams with different loadings of cardanol. The effects of cardanol on the properties of prepolymer and phenolic foams were studied.

The addition of cardanol increases the viscosity of prepolymer, which was obvious when the dosage of cardanol was over than 5 wt %. The apparent density results showed that when the dosage of cardanol was 5 wt %, the modified foams obtained lowest apparent density. Through the SEM results, with the increase of cardanol, some cells with increasingly large size existed, which indicated that the combination of cells in cure process increased. With respect to the mechanical properties, phenolic foams with 5 wt % cardanol had slight improvement on the mechanical performance. Noticeably, phenolic foams modified by 10 wt % cardanol increased by 22% in flexural strength and 28% in bending modulus compared to pure phenolic foams, which indicates that the incorporation of cardanol does improve the toughness of phenolic foams. When the dosage of cardanol was 15 wt %, the mechanical performance of modified foams deteriorated. As to the thermal stability, 5 wt % cardanol dosage could improve the thermal stability of phenolic

foams. Thermal stability of modified foams decreased with addition of cardanol over 5 wt %, compared to pure phenolic foams.

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