

Synthesis and Characterization of DOPO-g-CNSL and Its Effect on the Properties of Phenolic Foams

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> Abstract: In order to improve the mechanical properties without reducing its flame retardancy of phenolic foams (PFs), 9, 10-dihydro-9-oxa-10phosphaphenanthrene-10-oxide (DOPO) was introduced in the structure of cashew nut shell liquid (CNSL) to improve its flame retardant, and the product of DOPO grafting CNSL (DOPO-g-CNSL) was obtained to modify phenolic resin, and to prepare DOPO-g-CNSL modified PFs (DCMPFs). The structures of DOPO-g-CNSL were verified by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (1H-NMR). Compared with CNSL, thermal stability of DOPO-g-CNSL was decreased and T_i decreased by 3.53%, but the residual carbon (800°C) was increased by 35.05%. Compared with pure PF, the mechanical properties, toughness and flame retardancy of DCMPFs were increased when the ratio of DOPO-g-CNSL to phenol (DOPO-g-CNSL/P) was no more than 10%. With the dosage of DOPO-g-CNSL/P increased, T_i of DCMPFs was slightly increased, but the carbon residues (800°C) were almost unchanged. And the cell sizes of DCMPFs were basically the same as the pure PF. By comprehensive analysis, the suitable dosage of DOPO-g-CNSL/P was no more than 10%.

Keywords: DOPO; CNSL; modification; phenolic foams; characterization

1 Introduction

As a thermal insulation material, phenolic foam (PF) has some excellent properties, such as excellent flame retardant, low smoke and low toxicity, and is widely used in many different fields including aviation, construction, industrial pipelines, transportation and so on [1-3]. Nevertheless, PF's large-scale promotion and application is greatly restricted because of its fragility [3-5]. The toughening modification for PF is imperative to decline its fragility. Glass fibers and aramid fibers (petroleum based products) were introduced in PF to improve the its toughness [6-8]. Polyurethane prepolymer [9], epoxy [3] and cardanol [10] (long and flexible molecular chains) were also introduced into the molecular structure of PF to reduced its fragility. Hereunder, the compounds with long and flexible molecular chains could be considered as a toughing agent for PF.

As a natural product, cashew nut shell liquid (CNSL) can be obtained from cashew husk by extraction. The main structure of CNSL contains a benzene ring and a long side-chain (15 carbons) with 0~3 double bonds, which named saturated, monoene, diene, and triene [11]. Therefore, CNSL has the characteristics of phenolic compounds and the flexibility of aliphatic compounds, which can be used to modify for phenolic resin (PR) and PF to improve the toughness of PR and PF [12-15]. However, the thermal stability and flame retardancy of PR and PF were decreased to some extent [16]. Since CNSL is not a flame retardant material, the modification for CNSL using flame retardant is necessary with the aim to improve the toughness of PF without reducing its flame retardancy.

As one of the excellent flame retardants, 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is mainly exerts the fire retardant quenching effect by releasing free PO radicals and terminating the

chain reaction of combustion in gas phase [17]. The P-H bonds of the structure in DOPO are very active, which is prone to result in the reaction of nucleophilic addition. Therefore DOPO was widely used in the field of flame retardant modified polymers [18-23].

Herein, this work aims to introduce phosphorus compound into the structure of CNSL to modify PR and PF. It was hypothesized that it could not only improve the mechanical properties of PF, but also without reducing its flame retardancy. The structure of DOPO-g-CNSL was characterized by fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (¹H NMR) spectroscopy, and the heat resistance was also tested by thermal gravimetric analyzer (TGA). The properties of DOPO-g-CNSL modified PFs were measured including the mechanical and fragile properties, flame resistance, heat resistance and microstructure as well.

2 Experimental

2.1 Chemicals and Reagents

Phenol (P, >99%), formaldehyde (37wt%), calcium oxide (CaO), and sodium hydroxide (NaOH) were obtained from Nanjing Chemical Reagent, Ltd. 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was obtained from Shenzhen jinlong chemical technology Co., Ltd. Polysorbate-80, petroleum ether and Paraformaldehyde (\geq 95%) were obtained from Sinopharm group Chemical Reagent Co. Ltd. Mixed acid curing agent and cashew nut shell liquid (CNSL) were obtained from Institute of Chemical Industry of Forestry Products, Chinese Academy of Forestry.

2.2 Synthesis of DOPO-g-CNSL

DOPO (4.32 g, 0.02 mol, 2 equiv) was added into a round bottom flask equipped with magnetic stirring at 150°C under nitrogen. CNSL (3.04 g, 0.010 mol, 1 equiv) was added in reactor when DOPO was melted. And then the reaction was performed for 9 h at 150°C under an inert environment (N_2). After the temperature decreased to 60°C, the vacuum filtration was performed and tetrahydrofuran (20 mL) was added and obtained a crude DOPO-g-CNSL. The wash of crude DOPO-g-CNSL with tetrahydrofuran and vacuum filtration was repeated three times, and obtained the viscous product (DOPO-g-CNSL). The final DOPO-g-CNSL was obtained after the dry at 40°C to a constant weight under vacuum.



Figure 1: Scheme of DOPO-g-CNSL

2.3 Preparation of DOPO-g-CNSL Modified Phenolic Resin (PR) and PF

PR was synthesized according to the literature [24]. During the processing of synthesis of PR, DOPOg-CNSL was introduced in the system of reaction, the ratio of DOPO-g-CNSL to phenol (DOPO-g-CNSL/P) were 5 wt%, 10 wt% and 15 wt% respectively. After the end of the reaction, DOPO-g-CNSL modified PR (DCMPR) was obtained. Surfactants (Polysorbate-80, 8%/DCMPR), acid curing agents (20%/DCMPR) and blowing agents (petroleum ether, 5%/DCMPR) were added into the DCMPR and completely mixed, which was then poured into a mold. DOPO-g-CNSL modified PF (DCMPF) was obtained after foaming for 1 h at 70°C.



Figure 2: Scheme of DCMPR

2.4 FT-IR Spectroscopy

FT-IR spectra of DOPO, CNSL and DOPO-g-CNSL were monitored by a Fourier transform infrared spectrometer (Nicolet IS10, America).

2.5¹H NMR Spectroscopy

¹H NMR spectra were performed on a DRX 500 NMR spectrometer (400 MHz) (Bruker, Germany) at room temperature using dimethyl sulfoxide as solvent, and tetramethylsilane (TMS) as an internal reference.

2.6 Thermogravimetric Analysis (TGA)

TGA curves were collected by a NETZCSH TG 209 F3 TGA system under nitrogen atmosphere. Samples were heated from 40°C to 800°C at a heating rate of 10°C/min.

2.7 Mechanical Properties Tests

Compression strengths and bending strengths were measured according to the standard ISO 844:2014 and ISO 1209-1:2012 respectively. The test was repeated for 5 times.

2.8 Fragility Tests

Fragility of PFs were determined in accordance with ISO 6187-2001; the samples used for the test were $25 \times 25 \times 25 \text{ mm}^3$, each group was twelve, tested three sets of samples, and took the average of three times results.

2.9 Limiting Oxygen Indexes (LOIs) Tests

LOIs of all samples were obtained at room temperature on a JF-3 LOI instrument (LOI analysis instrument company, Jiangning County, China) according to ISO 4589-1-2017, the number of tests was five.

2.10 Microstructure Analysis

Scanning electron microscope (SEM) was used to observe the micro morphology of PFs by a Hitachi S 3400-N scanning electron microscope.

3 Results and Discussion

3.1 FT-IR of DOPO-g-CNSL

As shown in Fig. 3, the FT-IR analysis of DOPO [25-27]: 2384.9 cm⁻¹ (P-H); 1608 cm⁻¹, 1589.6 cm⁻¹ and 1559 cm⁻¹ (phenyl); 1446.3 cm⁻¹ (P-phenyl). The FT-IR analysis of CNSL [10,14]: 3345.5 cm⁻¹ (phenyl-OH); 2926.2 cm⁻¹ (-CH₂-) and 2853.6 cm⁻¹ (-CH₃) in the side chain of CNSL; 995.4 cm⁻¹ and 722.1 cm⁻¹ (-C=C-) in

the side chain of CNSL. Compared with the FT-IR spectrum of DOPO, the characteristic peak of P-H (in DOPO-g-CNSL) disappeared at 2384.9 cm⁻¹. And compared with the FT-IR spectrum of CNSL, the chemical groups (-CH₂- and -CH₃) were identified in the FT-IR spectrum of DOPO-g-CNSL by the peaks at 2927.4 cm⁻¹ and 2855 cm⁻¹, and the peaks (995.4 cm⁻¹ and 722.1 cm⁻¹) had reduced in size in the spectrum of the DOPO-g-CNSL, which indicated that some degree of grafting reaction had taken place through the double bonds in the aliphatic side chain of the CNSL. From the FT-IR analysis, it was evident that DOPO-g-CNSL was successfully synthesized.



Figure 3: FT-IR of DOPO-g-CNSL

3.2¹H NMR of DOPO-g-CNSL

For further confirmation of molecular structure, ¹H NMR spectrum of DOPO-g-CNSL were recorded and shown in Fig. 4. For DOPO, the signal around 6.56 to 8.86 ppm was corresponded to the phenyl protons [28-31]. For CNSL, the chemical shifts of H^a, H^b, H^c, H^d and H^e were observed at 0.97 ppm, 1.38 ppm, 2.10 ppm, 1.64 ppm and 2.60 ppm respectively, and the signal around 5.44 ppm (H^f) was corresponded to double bonds protons [10]. For DOPO-g-CNSL, the chemical shifts of H^a', H^b', H^c', H^d', H^e' and H^g' were observed at 0.92 ppm, 1.33 ppm, 2.07 ppm, 1.61 ppm, 2.54 ppm and 2.83 ppm respectively. The protons of the long side-chain appeared in the spectrum of DOPO-g-CNSL. These results supported that the reaction occurred between DOPO and CNSL.



Figure 4: ¹H NMR spectra of DOPO-g-CNSL

3.3 TGA of DOPO-g-CNSL

Fig. 5 shows TG and DTG of DOPO-g-CNSL. The initial decomposition temperatures (T_i) [32] of DOPO, CNSL and DOPO-g-CNSL were 283.3°C, 277.3°C and 267.5°C respectively, and the carbon residues (800°C) were 5.49%, 2.71% and 3.66% respectively. It was observed that T_i of DOPO-g-CNSL was less than that of CNSL, but the carbon residue (800°C) of DOPO-g-CNSL was more than that of CNSL. The result showed that there was no positive significance to improve the heat resistance of DOPO-g-CNSL. However, the carbon residue (800°C) (3.66%) of DOPO-g-CNSL was more than that of CNSL (2.71%). Since, biphenyls heterocycle was introduced in the molecular structure of CNSL by modification, and led

to the increase of the carbon content of DOPO-g-CNSL. However, the carbon residue (800°C) of DOPO-g-CNSL was slightly improved.



Figure 5: TG and DTG of DOPO-g-CNSL

3.4 Compression and Bending Strength of DCMPFs

Compression and bending strength of DCMPFs show in Fig. 6. With the increasing of the dosage of DOPO-g-CNSL/P, the compression and bending strengths of DCMPFs were firstly increased and then decreased. When the amount of DOPO-g-CNSL/P was 10%, the compression and bending strengths of DCMPFs were more than others'. And the compression and bending strength of DCMPFs were more than those of pure PF. It could be explained that DOPO-g-CNSL had a long side chain, when it was introduced into PFs, the toughness and intensity of DCMPFs were improved. Therefore, the capacity of resistance compressive and bending were increased and were significantly better than that of pure PF. However, with the dosage of DOPO-g-CNSL/P increased, the damage for the cell structures of DCMPFs were gradually revealed (Fig. 10), and the effect of destruction on the cell structure of DCMPFs was gradually greater than that of toughness, so the mechanical properties of DCMPFs were deteriorated. Therefore, the suitable dosage of DOPO-g-CNSL/P was no more than 10%.



Figure 6: Compression and bending strength of DCMPFs

3.5 Fragility of DCMPFs

Fragility is one of the most important index, which can use to characterize the toughness of foams. The ratio of mass loss is generally used to reflect its good or bad of the fragility or toughness of foams. The better toughness of foam is, the less ratio of mass loss is. The fragilities of DCMPFs show in Fig. 7. When the content of DOPO-g-CNSL/P was 5%, the ratios of mass loss of DCMPFs were slightly increased. However, with the increase of dosage of DOPO-g-CNSL/P, the ratios of mass loss of DCMPFs were firstly decreased, and then increased. When the dosage of DOPO-g-CNSL/P was 10%, the ratio of mass loss of DCMPFs was the lowest, and was less than that of pure PF. The reason could be explained that the

toughness of DCMPFs were improved by introducing DOPO-g-CNSL into PFs. However, with the dosage of DOPO-g-CNSL/P increased, the original bubble structure was destroyed and the bubble uniformity was decreased (Fig. 10), the toughness of DCMPFs was fail. Therefore, the ratio of mass was increased [30]. The results showed that the content of DOPO-g-CNSL/P was not too much, the better dosage of DOPO-g-CNSL/P was no more than 10%.



Figure 7: Fragility of DCMPFs

3.6 Limited Oxygen Index (LOI) of DCMPFs

As shown in Fig. 8, LOIs of DCMPFs were gradually increased with the increase of the content of DOPO-g-CNSL/P, and were more than that of pure PF. LOIs were in the range of 38.2% to 44.0%, so all the foams were considered as the flame resistant materials (LOI \geq 27%) [33]. The results showed that it was positively improve LOIs of DCMPFs by introducing DOPO-g-CNSL into PFs. This could be explained that the phosphorus element (in DOPO-g-CNSL) was introduced into DCMPFs during the process of combustion, the fire retardant quenching effect could be exerted by releasing free PO radicals and terminating the chain reaction of combustion in gas phase [17]. Therefore, LOIs of DCMPFs were more than that of pure PF. And with the dosage of DOPO-g-CNSL/P increased, there was more and more flame retardants introduced into PFs, LOIs were improved slightly.



Figure 8: LOI of DCMPFs

3.7 TGA of DCMPFs

Fig. 9 shows TG and DTG of DCMPFs. The initial decomposition temperatures (T_i) [32] of pure PF and DCMPFs were 194.0°C and the carbon residue (800°C) was 51.61%. With the dosage of DOPO-g-CNSL/P increased, T_i of CPFs were 196.1°C, 200.1°C and 205.6°C respectively. The carbon residue (800°C) were 51.00%, 50.08% and 51.20% respectively. Compared with pure PF, T_i of DCMPFs was slightly increased, but the carbon residues (800°C) were slightly decreased. It might be explained that T_i of DOPO-

g-CNSL (267.5°C, in Fig. 5) was more than that of DCMPFs, otherwise, phosphorus (in DOPO-g-CNSL) was introduced into the DCMPFs, which could migrate to the external char layer, form a thick and compact thermal barrier when the DCMPFs were flamed or heated, which covered on the surface of DCMPFs prevented oxygen and heat getting into the foams, further enhanced the thermal stability of DCMPFs [34-38]. Although, the introduction of phosphorus was conducive to carbon formation. Nevertheless, the carbon residues (800°C) of DOPO-g-CNSL was very low (3.66%, in Fig. 5), the carbon residues (800°C) of DCMPFs were slightly decreased, but not much. The result showed that there was positive significance to improve the heat resistance of DCMPFs, and it was also auxiliarily certified the reason was that the flame retardant of DCMPFs was gradually increased with the dosage of DOPO-g-CNSL/P increased. However, there was positive significance to improve the heat resistance of CPFs at high temperature.



Figure 9: TGA of DCMPFs

3.8 SEM of DCMPFs

Fig. 10 shows SEM micrographs (50×) of DCMPFs. The cell size of pure PF was about at 200~400 µm. With the addition of DOPO-g-CNSL/P increased, the cell size of DCMPFs was slightly increased. When the addition of DOPO-g-CNSL/P was less than or equal to 10%, the cell size of DCMPFs was about at 200~400 µm except a very few large cells size was about 400-500 µm. When the addition of DOPO-g-CNSL/P was equal to 15%, the cell size was about at 300~800 µm. The results showed that when the dosage of DOPO-g-CNSL/P was less than or equal to 10%, there was less effect on the cell structure of DCMPFs when DOPO-g-CNSL was introduced in PFs, so the cell sizes of DCMPFs were basically the same as the pure PF, and the cell distribution was relatively regular. With the amount of DOPO-g-CNSL/P increased, the destructive effect of DOPO-g-CNSL on the cell structure is gradually dominant, therefore, the size of cell was gradually increased. The results showed that the content of DOPO-g-CNSL/P was not too much, the better dosage of DOPO-g-CNSL/P was no more than 10%.



Figure 10: SEM micrographs of DCMPFs (a: 0%; b: 5%; c: 10%; d: 15%)

4 Conclusions

The structure of DOPO-g-CNSL was confirmed by FT-IR and ¹H NMR spectra. Additionally, compared with CNSL, the thermal stability of DOPO-g-CNSL was changed little, but the residual carbon (800°C) slightly increased. Compared with pure PF, when the dosage of DOPO-g-CNSL/P was no more than 10%, the mechanical properties of DCMPFs were increased, the ratios of mass loss were decreased. With the addition of DOPO-g-CNSL/P increased, LOIs heat resistance and the cell size of DCMPFs was slightly increased. By comprehensive analysis, the suitable dosage of DOPO-g-CNSL/P was no more than 10%.

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