Synthesis and Characterizations of a Latent Polyhedral Oligomeric Silsequioxane-Containing Catalyst and its Application in Polybenzoxazine Resin

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ABSTRACT: In this article, a novel latent curing agent, octa(paratoluenesulfonic acid ammomium salt) (OPAAS) polyhedral oligomeric silsequioxane was synthesized and used in modifying the polybenzoxazine/2,2'-(1,3-phenylene)-bis(4,5-dihydro-oxazoles) (PBO) (PBZ/PBO) resin. The liberated octa(aminophenyl) silsesquioxane and paratoluenesulfonic acid can catalyze the ring-opening reaction of benzoxazine (BZ) resin. The initial curing temperature (T_i), peak curing temperature (T_p) and the Enthalpy of the curing temperature had significantly decreased with respect to pristine BZ/PBO resin. When the OPAAS amount was 3 wt %, the peak curing temperature decreased from 233.7 to 218.2°C. Also, PBZ/PBO/OPAAS composites exhibited better storage modulus than pure PBZ/PBO resin. Meanwhile, PBZ/PBO/OPAAS composites are more thermally stable than PBZ/PBO resin. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: crosslinking; resin; thermal properties; thermosets

INTRODUCTION

Phenolic resins retain industrial and commercial interest a century after their introduction, despite the emergence of several new classes of thermosets and several new generation materials that are superior in some aspects, which ascribe to the good heat and flame resistance properties, and low cost[1] phenolic resins still find market in competition with epoxy and polyimide resins, especially serve as the thermo-structural material in aerospace and railway industry.[2,3]

The benzoxazine (BZ)-based family of phenolic provides interesting materials with good thermal properties and flame retardancy originated from phenolics, together with near-zero volumetric change upon curing, low water absorption, high char yield, weak acid catalysts required for curing, absence of byproducts during curing, mechanical performance, and molecular design flexibility of advanced composites.[4,5]

All of those properties make the polybenzoxazine (PBZ) a promising material in application. However, the high curing temperature serves as the bottleneck in industrial application. Meanwhile, the cross-link density of PBZ need to be further improved as to be a high performance material.

Many efforts were given to improve the performance of the BZ resin in the worldwide. Ishida and coworkers[6–9] synthesized a lot of types of BZ and studied the cure kinetics, molecular structures, mechanical, dynamic mechanical properties, and so on. Yagci and coworkers[10–12] synthesized a set of thermal curable polymer with BZ functionalities by new means, namely atom transfer radical polymerization, ring-opening polymerization and click chemistry reaction. An excellent review about PBZ in recent advancement were highlighted in Journal of Polymer Science: Polymer Chemistry by Yagci et al.[13]

Kimura et al. reported the synthesis and a set of latent catalysts of PBZ /PBO resin.[14–16] The latent catalysts of this study is consisted of the salts of acid and amine compounds, which would liberate the free acids and amines by high temperature
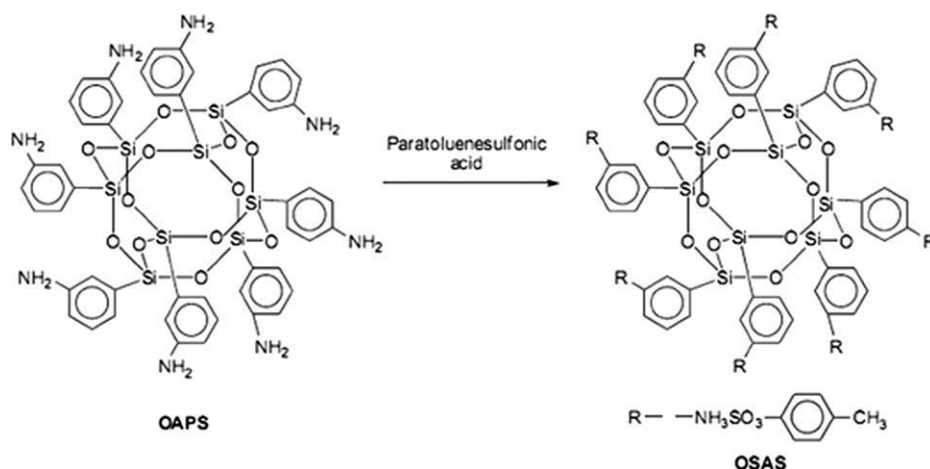
Scheme 1 The synthesis of OPAAS.

decomposition. The free acids and amines serve as the catalysts of the ring-opening reaction of the BZ/PBO resin. The PBZ/PBO resin exhibited higher cross-link density, especially, short curing time and lower the curing temperature. When the latent catalyst amount was 10 wt %, the peak curing temperature decreased from 234 to 162°C.

Polyhedral oligomeric silsequioxane (POSS) are compounds with organic–inorganic hybrid architecture. The rigid Si—O—Si framework provides unique heat resistance and excellent mechanical properties. Conversely, the vortex groups connecting to silicon increase the compatibility and processability with the polymer matrix.[17] POSS used to modify the thermoset resins by the chemical reaction of groups which was widely reported in recent years.[18–21]

BZ-POSS were prepared by hydrosilylation of vinyl-terminated BZ with the hydro-silane functional group of H-POSS by Feng-chih Chang and co-workers.[22] The nanocomposite copolymerized by BZ-POSS with BZ monomer exhibited improvement in thermal properties and glass transition temperature. However, higher amount of the BZ-POSS tend to aggregate due to the poor miscibility of the vertex group with matrix. In another Chang's article,[23] they synthesized a novel octafunctionalized POSS from VP-a and Q_8M_8H by a platinum complex catalyzed hydrosilylation, in which VP-a is defined as a vinyl-terminated BZ monomer, and Q_8M_8H is defined as octakis(dimethylsiloxy)-T8-silsequioxane. A new type of PBZ-POSS (multifunctional BZ POSS) nanocomposite was prepared by the cross-linking unit of MBZ-POSS, which undergoes polymerization with other BZ monomer. The higher POSS content result in the hybrids displaying apparently higher glass transition and thermal decomposition temperatures than that of the neat PBZ.

In our group, several kinds of POSS were used to modify the PBZ resin, namely octaaminophenyl POSS,[24,25] poly-benzoxazinyl functionalized POSS

(BZ-POSS),[26] epoxide octavinyl POSS,[27] and trisilanol POSS (T7POSS),[28] all of which exhibited better thermal and mechanical properties than pristine BZ resin.

Herein, we investigated a novel latent catalyst containing POSS, octa(paratoluenesulfonic acid ammomium salt) (OPAAS, as shown in Scheme 1), and its application into the BZ/PBO resin. The curing behavior, dynamic mechanical properties, and thermal stability of the BZ/PBO/OPAAS composites were researched in details as well.

EXPERIMENTAL

Materials

Bisphenol A-based BZ monomer was synthesized from bisphenol A, aniline, and paraformaldehyde by using a solvent method described in our previous article. Phenyltrialkoxysilane (>99.0%), aniline, para-formaldehyde, bisphenol A, tetrahydrofuran (THF), sodium hydrate (NaOH), paratoluenesulfonic acid, hydrazine monohydrate, and fuming nitric acid were of analytically pure grade and purchased from Beijing Reagent Co., China. THF was dried and distilled over CaH_2. All other reagents were used as received without further purification.

Characterizations

Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Nicolet Nexus 670 FTIR Spectrometer at room temperature (25°C) in the range of 4000–400 cm^{-1} at a resolution of 0.1 cm^{-1}. All samples were prepared as pellets using spectroscopic grade KBr.

Dynamic mechanical analyses were conducted on a Rheometrics Scientific^{TM} DMTA V at 1 Hz at heating rate of 5°C/min over the temperature range of room temperature to 300°C.
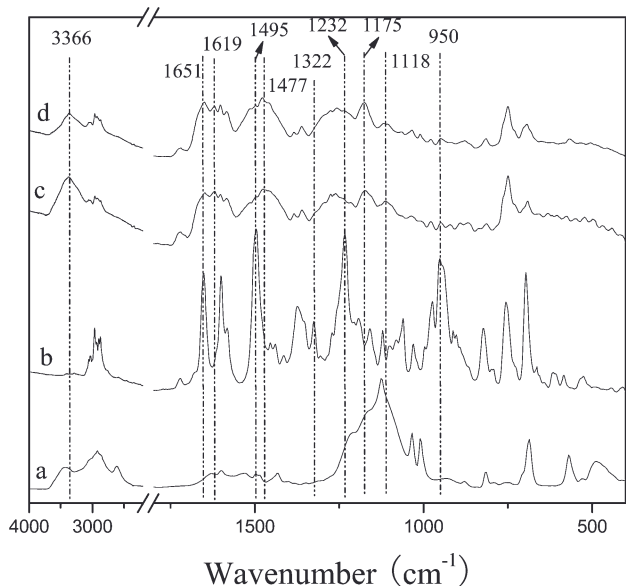
Figure 1 FTIR spectra of OPAAS (a), BZ/PBO mixture (b), PBZ/PBO after curing (c) and PBZ/PBO/OPAAS (OPAAS: 5 wt %) (d).

Thermogravimetric analyses (TGA) were performed with a Netzsch 209C thermogravimertric analyzer under nitrogen atmosphere from the ambient temperature up to 700°C at a heating rate of 20°C/min.

The syntheses of OPAAS POSS

Octa(aminophenyl) silsesquioxane (OAPS) was synthesized via the method according to our early report.[28] FTIR (KBr): 1124.88 cm^{-1} (Si—O—Si), 3221.97 and 3375.60 cm^{-1} (N—H), 1620.85 cm^{-1} (Ph—NH$_2$).[29] Si NMR (THF): $\delta = -78.61$.

At 1:8 molar ratio, paratoluenesulfonic acid was added dropwise to the solution of OAPS in THF at refluxing temperature. The solution was distilled by reduced pressure, and brown solid of OPAAS POSS was dried under vacuum. FTIR (KBr): 1124.86 cm^{-1} (Si—O—Si), 1034.36 and 1009.29 cm^{-1} (Si—Ph), 750.27 cm^{-1} (Ph—S), 2922.11 cm^{-1} (C—H, in benzene ring), and 3432.59 cm^{-1} (N—H, in —NH$_2$...HSO$_3^-$).

The preparation of PBZ/PBO/OPAAS composites

The same molar amount of PBO was added to BZ monomer in a 100 mL three-bottled flask equipped by a stirrer, condenser, and thermometer. The temperature was gradually increased to 140°C and the system was stirred until both the PBO had melted completely. Then, cooling to 100°C, the desired amount of OPAAS was added into the system. The PBZ/PBO/OPAAS was cured at 120°C for 1 h, 140°C for 1 h, 160°C for 2 h, 180°C for 3 h, 200°C for
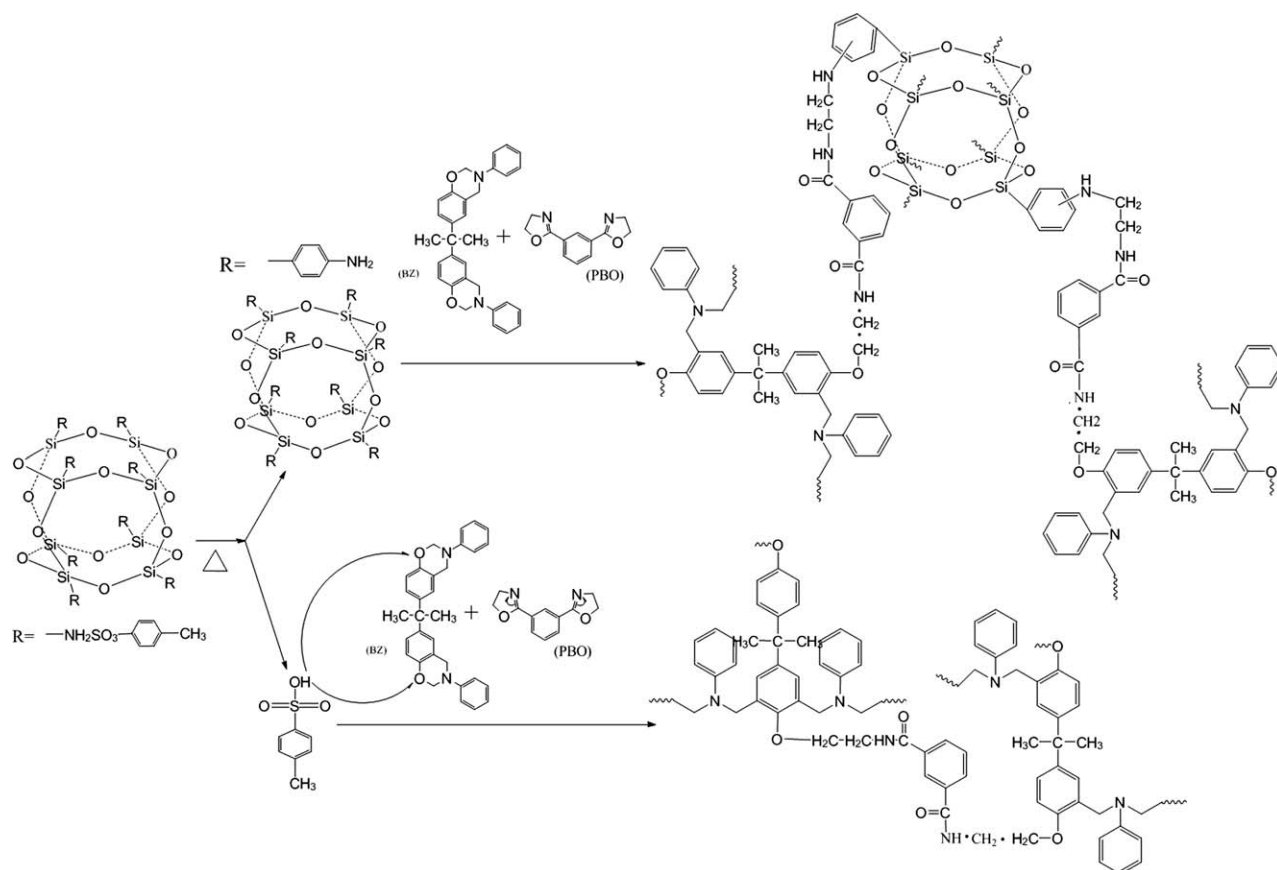
Scheme 2 Curing reaction of BZ/PBO with OAAPS.
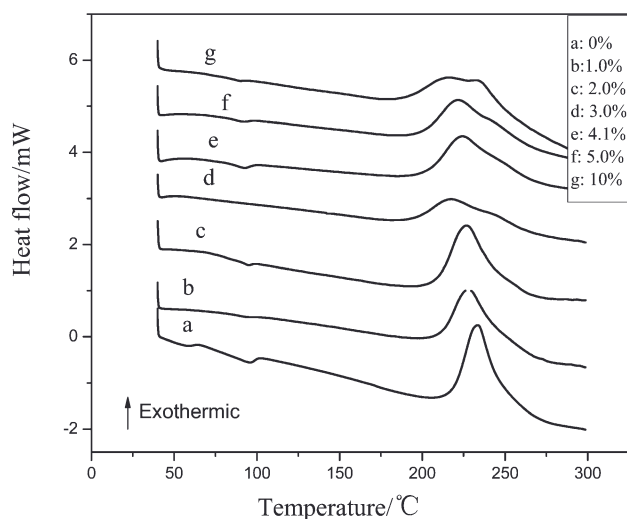
Figure 2 DSC curves of PBZ/PBO/OPAAS mixtures.

1 h, and 220°C for 1 h. Other mass ratio of BZ/PBO/OPAAS (100/1, 100/2, 100/3, 100/4, 100/5, and 100/10) were prepared in the same way.

RESULTS AND DISCUSSION

FTIR of PBZ/PBO/OPAAS system

As indicated in the Figure 1, FTIR was used to investigate the curing process of BZ/PBO/OPAAS system. In spectra b, 950, 1495, 1232, and 1332 cm^{-1} can be ascribed to the characteristic signal of BZ. It manifested that the absorption peak of BZ gradually decreased and then disappeared during the curing process. 1477 cm^{-1} in b, assigned to the characteristic absorption peak of trisubstituted benzene, moves to 1495 cm^{-1} in c and d after curing process. It can be seen that, the formation of tetrasubstituted benzene is generated by the ring opening reaction of the BZ. Meanwhile, 1651 cm^{-1} (characteristic peak of PBO) disappears in both c and d which imply the ring opening reaction of PBO during the curing process. The appearance of 3366 cm^{-1} in c and d represent the phenolic hydroxyl which formed by the ring opening reaction of BZ.

OPASS can be mixed into the PBZ/PBO system and may react at curing conditions. The possible scheme is shown in Scheme 2. OPAAS would release the free acids and amines by decomposition at high temperature. The free para-toluenesulfonic acid serves as the catalysts of the ring opening reaction of the BZ-PBO resin, while OAPS can be incorporated into the composites by the reaction among amine group in OAPS, BZ, and PBO.

The curing behavior of PBZ/PBO/OPAAS composites

As shown in Figure 2 and Table I, the DSC curves indicate the peak curing temperature of pure BZ-

TABLE I
DSC Results of BZ/PBO/OPAAS Mixtures

OPAAS (wt %)	Curing temperature (°C)		ΔH (J/g)
	T_i	T_P	
0	192.7	233.7	283.9
1.0	183.2	228.2	276.1
2.0	181.6	227.0	279.8
3.0	171.2	218.2	201.5
4.0	177.5	224.5	286.3
5.0	177.5	222.1	295.7
10	177.8	233.7	346.3

PBO at 233.7°C, while all the BZ-PBO-OPAAS composites display a decreased T_P. The lowest value of T_P appears at 218.2°C and T_i decreases from 192.7°C (pure BZ-PBO) to 171.2°C, when the mass ratio of the OPAAS is 3%. Those results suggest that OPAAS serves as the potential curing catalyst to reduce the curing temperature. The mechanism may be ascribed into the para-toluenesulfonic and OAPS which are derived from the OPAAS when exposed to high temperature. According to the literatures, the para-toluenesulfonic and ammomium salt stemming from para-toluenesulfonic acid ammomium salt can catalyze the ring-opening reaction of BZ and PBO and reduce the curing temperature.
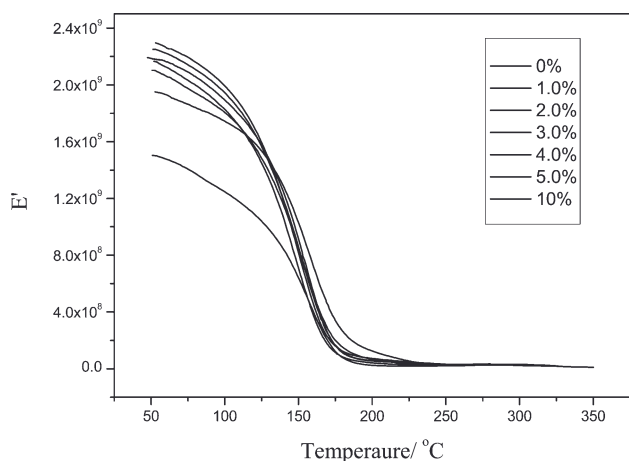
Dynamic mechanical properties of PBZ/PBO/OPAAS composites

As indicated in Figure 3, the T_g of the pure PBZ-PBO composite is 179°C, which is higher than the T_g of PBZ-PBO-OPAAS nanocomposite. The reason
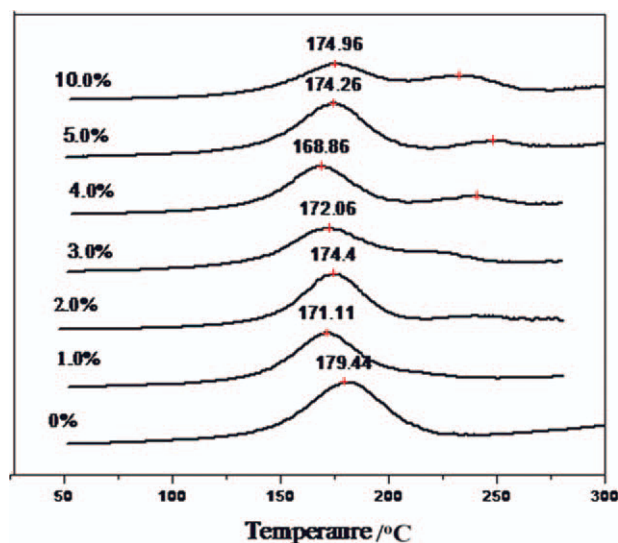
Figure 3 Tan δ as a function of temperature of PBZ/PBO/OPAAS composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

Figure 4 The storage modulus as a function of temperature of PBZ/PBO/OPAAS composites.

might be the increasing volume formed by OAPS reacting with para-toluenesulfonic so that the mobility of polymer chain improves. A part of OPAAS particles aggregated in the network of matrix act as the fillers which decreases the glass transition temperatures of PBZ-PBO-OPAAS composites.

Figure 4 exhibits the storage modulus in 100°C of pristine PBZ/PBO resin and PBZ/PBO/OPAAS composites with different OPAAS amount. Composites exhibited the higher storage modulus as the OPAAS amount increases first and then followed by a decrease when the amount is more than 4%. The highest storage modulus is displayed at 2.00 GPa when the mass ratio is 4%. This can be ascribe to the liberated OAPS, as the crosslink agent gets involved into the main chain reaction and improve the crosslink density of matrix. Meanwhile, the cage structure of Si—O—Si enhance the rigidity of the matrix which lead to the improvement of storage modulus of PBZ/PBO/OPAAS composites.

Thermal stability properties of PBZ/PBO/OPAAS composites

TGA curves of PBZ/PBO/OPAAS composites were shown in Figure 5, the temperature of 10% weight loss and char yield in 700°C was summarized in

TABLE II
Dynamic Mechanics Properties of PBZ/PBO/OPAAS Composites

OPAAS (%)	T_g (°C)	E' (Pa)/10^9 (100°C)
0	179.4	1.25
1.0	171.1	1.83
2.0	174.4	1.89
3.0	172.1	1.95
4.0	168.9	2.00
5.0	174.3	1.80
10.0	174.9	1.74

TABLE III
TGA Results of PBZ/PBO/OPAAS Composites

OPAAS (%)	The temperature of 10 wt % loss (°C)	Char yield in 700°C (%)
0	368.4	43.1
1.0	385.3	44.1
2.0	377.7	43.1
3.0	371.7	41.0
4.0	378.0	41.5
5.0	377.0	40.2
10.0	375.2	45.2

Table II. As illustrated in Table II, the value of 10% weight loss temperature significantly increased from 368.4°C in the pure PBZ/PBO resin to 385.3°C when the amount is 1.0%. The char yields of PBZ/PBO/OPAAS composites are roughly equal to pristine PBZ/PBO resin. In general, all the composites exhibit higher thermal decomposition temperature and char yield. The improved thermal stability of pristine PBZ/PBO resin can be interpreted by the relationship of structure and properties of composites.

The curing behaviors of PBZ/PBO/OPAAS composites were investigated by FTIR, as we studied earlier. During curing process, OPAAS liberate OAPS which react with PBZ and PBO can improve the crosslink density of the matrix. The well-dispersed OAPS in matrix can retard the motion of segment which can enhance the thermal stability of PBZ/PBO resin. Thus, the initial degradation temperatures of composites are improved.

CONCLUSION

We have synthesized a novel latent curing agent OPAAS POSS and investigated its application in modifying the BZ/PBO resin. The liberate OAPS and paratoluenesulfonic acid can catalyze the ring-opening reaction of BZ resin. The initial curing temperature, peak curing temperature, and the Enthalpy of the curing temperature had significantly decreased than pristine BZ/PBO resin. When the OPAAS amount was 3 wt %, the peak curing temperature decreased from 233.7 to 218.2°C. PBZ/PBO/OPAAS composites exhibited better storage modulus than pure PBZ/PBO resin since OAPS liberated from OPAAS can act as crosslink agent to improve the crosslink density of matrix. Meanwhile, the stability properties of PBZ/PBO/OPAAS composites are roughly equal to pristine PBZ/PBO resin.

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