

Thermal Stability of Cocured Blends of Vinyl Trimethoxysilane and Aryl Acetylene Resins with Different Posttreatments

Yongsheng Wu, Ruobing Yu, Lin Hu, Qianqian Li, Changjin Zhu

Shanghai Key Laboratory of Advanced Polymeric Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China
Correspondence to: R. B. Yu (E-mail: rbyu@ecust.edu.cn)

ABSTRACT: Poly(aryl acetylene) (PAA) modified by vinyl trimethoxysilane (VTMS) was successfully prepared from a blend of diethynyl benzene (DEB) and VTMS. Scanning electron microscopy and Fourier transform infrared spectroscopy investigations showed that VTMS was copolymerized with DEB. Thermogravimetric analysis revealed that PAA modified by VTMS had a better thermooxidation stability than PAA. Through the application of postirradiation and posthydrolysis, the thermal stability in nitrogen and in air of PAA modified by VTMS was greatly improved. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40158.

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INTRODUCTION

Poly(aryl acetylene) (PAA) is a highly crosslinked aromatic material with excellent thermal stability and very high char yield at 800°C in nitrogen. PAA has been regarded as the best alternative to phenolic resins for matrices in high-temperature composite materials.^{1–3} PAA has many advantages, including fewer pores and volatiles due to curing by addition, higher char yields, and lower shrinkages during pyrolysis. Unfortunately, the direct curing of aryl acetylene (AA) is extremely exothermic and leads to severe shrinkage. PAA is also susceptible to decomposition at elevated temperatures in oxidative environments.^{4–6} It is well known that siloxane-containing polymers have many outstanding properties, such as good flexibility, high heat resistance, and excellent oxidation resistance.^{6–8} Therefore, to improve the thermooxidative stability of PAA, more and more researchers have focused on the modification of PAA through the introduction of Si.^{7–22}

In recent years, silicon-containing poly(aryl acetylene)s (MSPs) have been synthesized; they are used in composite materials, ceramic materials, and electronic materials.^{7–10} Itoh and coworkers^{8–10} obtained MSP oligomers by dehydrogenative coupling polymerization reactions between phenylsilane and *m*-diethynyl benzene (*m*-DEB). The residue yield of cured MSP at 1000°C under argon was 94%, and the temperature at 5% weight loss (T_{d5}), determined by a thermogravimetric analysis (TGA) trace, was 860°C under argon.⁹ In 2001, phenyl acetylene terminated poly(silyleethynylene phenyleneethynylene) oligomers were synthesized by a condensation reaction between dichloro-

silane and a mixture of diethynyl benzene (DEB) and phenyl acetylene magnesium reagents. The cured phenyl acetylene terminated poly(silyleethynylene phenyleneethynylene) oligomers possessed high heat resistance and high char yield.¹¹ Huang et al.¹² prepared a series of AA oligomers with siloxane units through condensation reactions of *m*-DEB magnesium reagents with various α,ω -bis(chloro)dimethylsiloxanes. The cured resins showed characteristics of high thermal stability. The residue yields at 1000°C were 72–86%, and the T_{d5} was 505–602°C under nitrogen. In air, the residue yields at 1000°C were 36–49%, and the T_{d5} was 514–548°C. As shown by the previous studies, the synthesis of MSP oligomers is complicated and dangerous and results in a low yield (only 60–70%).⁶

To explore an easy way to introduce silicon into PAA, the blending of AA and silane before a thermal reaction was used to modify PAA, which was absent because of the poor miscibility between the AA and some silane monomers. In this study, we chose vinyl trimethoxysilane (VTMS) to blend with AA monomer. The miscibility of the blends and the cured samples from the blends were investigated. As the curing of AA is done by addition, posttreatment at high temperature is a common way to its improve properties. However, at high temperature, PAA is prone to oxidation; this is crucial to its comprehensive properties. Posthydrolysis and postirradiation can be done at low temperature and have so far not been applied to PAA.

In this study, we examined the effect of VTMS on the cured samples and investigated the thermal properties of the cured samples after irradiation and hydrolysis. There were three goals:

(1) to investigate the thermal stability and char yield of the cured samples from the blend of VTMS and AA (the cured samples), (2) to analyze the thermal properties and char yield of the cured samples after hydrolysis, and (3) to irradiate the cured samples and measure their thermal properties.

EXPERIMENTAL

Materials

The AA monomer was DEB, a mixture of *p*-diethynyl benzene (*p*-DEB) and *m*-DEB (*p*-DEB = 24.7% and *m*-DEB = 75.3%), supplied by East China University of Science and Technology.

VTMS (chemically pure) was supplied by Tianjin Chemical Reagent Institute.

Preparation of the Blends

DEB and VTMS, weighed according to the designed composition, were stirred vigorously at 70°C in a beaker for 30 min to obtain the final blend.

Thermal Cure of the Blends

The blends were thermally cured in an oven with the following protocol: 90°C for 2 h, 110°C for 4 h, 130°C for 20 h, 150°C for 4 h, 180°C for 4 h, 200°C for 4 h, and 250°C for 2 h. Then, the cured samples were cooled slowly to room temperature. Shiny void-free and dark cured resins were obtained, and we called them the cured samples or PAA-VTMS.

Posthydrolysis of the Cured Samples

The cured sample was milled into a fine powder, and the powder was put into boiling water for some time. The powder after hydrolysis was filtered and put into an oven to dry.

Postirradiation of the Cured Samples

The cured sample was put into a test tube, and the tube was closed to be used for postirradiation. Irradiation was conducted at room temperature, and the absorbed doses were 10, 50, and 100 kGy with ⁶⁰Co, respectively.

Instrumental Measurements

Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 5700 in the form of pellets with KBr. TGA was performed on a Netzsch STA 409 thermal analyzer at a heating rate of 10°C/min under air or N₂ from 25 to 800°C. Scanning electron microscopy (SEM) study was done on a field emission scanning electron microscope (S-4800), produced by Hitachi, Ltd.

Degree of Curing

The cured sample was ground into a powder, and 1 g of powder was weighed. Second, the sample was put into a Soxhlet extractor with the leaching liquor of acetone. The extraction time (*t*) in hours was calculated by eq. (1):

$$t = (\text{Number of the sample}) + 1(\text{h}) \quad (1)$$

After extraction, the dried sample was weighed (*w*₁). The curing degree (*K*) was calculated according to eq. (2):

$$K = (w_1/1) \times 100\% \quad (2)$$

RESULTS AND DISCUSSION

Blend Miscibility

The properties of polymer blends are always governed by the miscibility of the components, which range from complete mis-

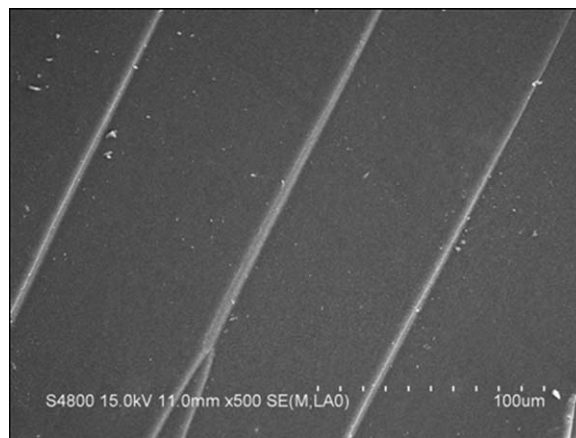


Figure 1. SEM micrograph of the PAA-VTMS blend (DEB/VTMS = 10:5).

cibility to phase separation.¹² Miscibility, a function of the interaction of polymer molecules in the blend, can be detected by various methods.^{13,14} In this study, the miscibility of PAA-VTMS was characterized by SEM. Figure 1 shows the SEM micrograph of PAA-VTMS (DEB/VTMS = 10:5), which existed as a monophasic structure. We observed that the cured samples had smooth cross-sectional surfaces and exhibited a typical brittle feature.

Because the indices of refraction of DEB and VTMS were different (at 30°C, the refractive index for DEB was 1.6375, and the refractive index for VTMS was 1.3920), transparency was an indication of miscibility. During the period of experimental temperatures, the blends and cured samples from the blends with varied VTMS contents were transparent; this implied that there was no visible phase separation in the melt, gel, or cured solid.

Degree of Curing of the Cured Samples

The degree of curing had an effect on the final properties of the materials. The degree of curing of the cured samples were studied, and the results follow.

As shown in Table I, the curing degree of the cured samples were above 97%; this indicated complete polymerization under the curing protocol. Because the monomer and silane homopolymer in the cured powder were soluble in acetone and could be leached by acetone,²³ the powder remaining after extraction was PAA and the copolymer of VTMS and DEB, not the monomer and homopolymer of VTMS; this showed that the introduction

Table I. Degree of Curing Results

DEB/VTMS mass ratio	Degree of curing (%)	DEB (mass %) ^a
10:0	99.1	100
10:1	97.4	91
10:3	98.1	76.9
10:5	98.1	66.7

^a DEB (mass %) = (Quality of DEB)/(Total mass).

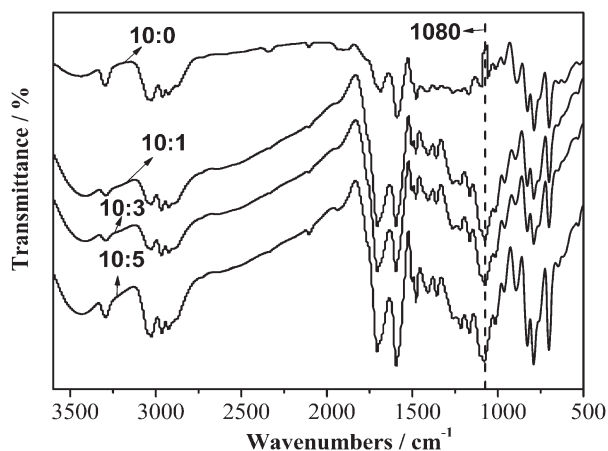


Figure 2. FTIR spectra of the cured samples.

of silicon into PAA was successful. Figure 2 presents the FTIR spectra of the cured samples that were extracted by acetone.

In Figure 2, a new characteristic absorption peak at 1080 cm^{-1} appeared, associated with Si—O—C, compared with the spectrum of the pure PAA. The FTIR spectrum was also proof of copolymerization between VTMS and DEB.

Thermal Stability of the Cured Samples

Thermal stability plays an important role in the application of PAA. PAA–VTMS is a dark brown–red, transparent, and brittle solid. The thermal stability of PAA–VTMS was evaluated by TGA in N_2 and air up to 800°C . Figure 3 describes the TGA profiles of the cured sample (PAA–VTMS) in N_2 .

As shown in Figure 3, the char yield of the cured samples with different compositions (DEB/VTMS) at 800°C in nitrogen were above 75%. The T_{d5} of the cured samples were above 410°C in N_2 . With increasing proportion of VTMS, the residue of the cured samples at 800°C and T_{d5} of the cured samples decreased. Because of the introduction of VTMS in PAA, the decomposition rate of the cured samples was different. The decomposition rate with a ratio of 10:5 DEB/VTMS was the fastest.

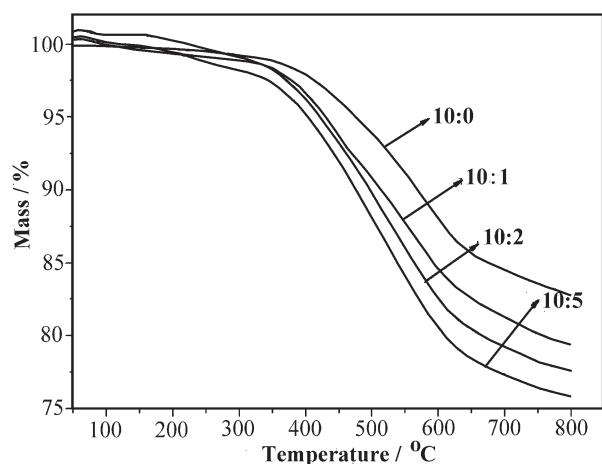


Figure 3. TGA profiles of the cured samples with different compositions (DEB/VTMS) in N_2 .

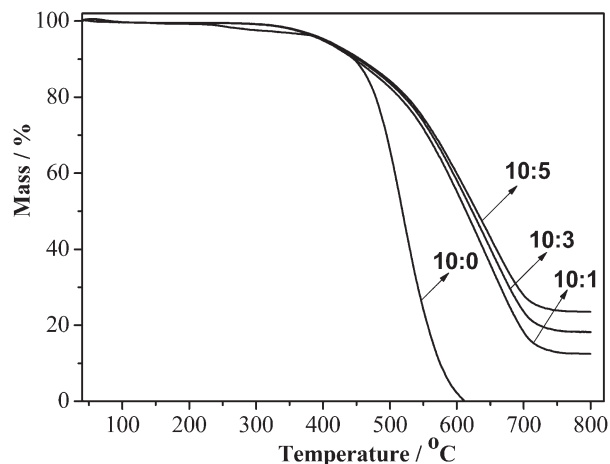


Figure 4. TGA profiles of the cured samples with different compositions (DEB/VTMS) in air.

With the introduction of the Si—O—C structure in the cured samples, the first bond breaking in the cured samples was that of the side-chain Si—O—CH₃ of silane during the process of pyrolysis. When more VTMS was present, the decomposition rate was faster and the char yield was lower in N_2 .

Thermooxidative Stability of the Cured Samples

The thermooxidative stability was also very important. In this study, TGA was used to evaluate the thermooxidative stability of the cured samples. Figure 4 shows the TGA profiles of the cured samples with different compositions (DEB/VTMS) in air. As expected, the stability in air was generally less than that in N_2 . The T_{d5} values for the cured samples were around at 402°C . With increasing VTMS, the char yield of the cured samples in air at 800°C ranged from 0 to 23.6%. Table II shows the results of the thermooxidative stability of the cured samples (data from Figures 3 and 4). The cured samples (PAA–VTMS) had better thermooxidative stability than PAA.

Thermal Properties of the Cured Samples after Irradiation Processing

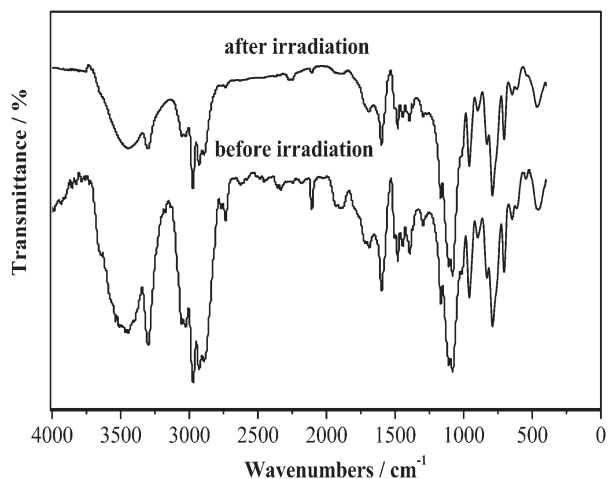
To improve PAA, postirradiation was applied to the cured samples modified by different proportions of VTMS. TGA was used to evaluate the thermal stability of the cured samples by postirradiation. The effects of the postirradiation dose on the cured samples could be concluded from Table III: (1) the thermal stability of the cured samples was greatly improved by postirradiation; (2) as the radiation dose increased, the thermal decomposition temperature of the cured samples increased; and

Table II. Thermooxidative Stability of the Cured Resin

DEB/VTMS mass ratio	$T_{d5\%}$ ($^\circ\text{C}$)		Char yield at 800°C (%)	
	In N_2	In air	In N_2	In air
10:0	475	402	82.8	0
10:1	430	405	79.5	12.5
10:3	421	404	77.6	18.2
10:5	402	404	75.8	23.6

Table III. Influence of Postirradiation on the Cured Samples (PAA–VTMS) in N₂

DEB/VTMS mass ratio	$T_{d5\%}$ (°C)				Char yield at 800°C (%)			
	0 kGy	10 kGy	50 kGy	100 kGy	0 kGy	10 kGy	50 kGy	100 kGy
10:0	475	486	495	499	82.8	83.2	83.6	83.8
10:1	430	444	472	486	79.4	80.1	80.4	80.6
10:3	421	440	468	479	77.6	78.2	78.2	78.1
10:5	403	417	460	476	75.8	76.5	76.5	76.8

**Figure 5.** FTIR spectra of the cured samples (10:5 PAA/VTMS) before and after postirradiation.

(3) the thermal decomposition temperature of PAA modified by VTMS (10:1) with radiation treatment (100 kGy) was 485°C in nitrogen, and the char yield was 80.6% in nitrogen.

When the cured samples were irradiated by ⁶⁰Co, the residual C≡C in PAA may have reacted. Figure 5 presents the FTIR spectra of the cured samples (10:5 PAA/VTMS) before and after postradiation. The peaks at 3294 and 621 cm⁻¹ corresponded to the absorptions of carbon–hydrogen stretching and bending vibrations. The C≡C stretching occurred at 2110 cm⁻¹. The absorption peak at 3290 cm⁻¹ revealed the presence of free terminal ≡C–H groups, and the absorption peak at 1700 cm⁻¹ indicated that PAA had a double-bond structure (–CH=CPh–). After irradiation, C≡C decreased.

Thermooxidative Stability of the Cured Samples after Irradiation Processing

The thermooxidative stability of the cured samples by postirradiation was explored by TGA (see Table IV). After the cured

Table IV. Influence of Postirradiation on the Cured Samples in Air

PAA/VTMS mass ratio	$T_{d5\%}$ (°C)				Char yield at 800°C (%)			
	0 kGy	10 kGy	50 kGy	100 kGy	0 kGy	10 kGy	50 kGy	100 kGy
10:0	402	413	422	432	0	0	0	0
10:1	420	426	438	444	12.6	12.9	13.5	14.3
10:3	404	414	438	453	18.2	18.8	19.8	20.6
10:5	403	420	450	461	23.5	24.2	25.6	26.3

Table V. Results for the Thermal Stability of the Cured Samples before and after Hydrolysis in N₂

DEB/VTMS mass ratio	$T_{d5\%}$ (°C)		Char yield at 800°C (%)	
	Before hydrolysis	After hydrolysis	Before hydrolysis	After hydrolysis
10:0	475	475	82.8	82.7
10:1	430	443	79.4	82.0
10:3	421	434	77.4	80.7
10:5	402	422	75.8	80.2

samples were treated by irradiation, the thermooxidative stability was better. When the ratio of DEB to VTMS was 10:5 and the radiation dose was 100 kGy, the decomposition temperature was 460°C, and the char yield at 800°C was 26.3% in air (PAA = 0%). The decomposition temperature of postirradiated PAA–VTMS was 60°C higher than that of the cured samples, and the char yield was 3% larger than that of the cured samples (Table IV was compared with Figure 4 and Table II). Postirradiation was helpful for improving the thermooxidative stability of the cured samples.

Thermal Properties of the Cured Samples that Were Hydrolyzed

In the cured samples, there were some methoxy groups (O–CH₃) that affected the thermal properties. The hydrolyzation of methoxy groups may be an effective way to improve the thermal stability of cured samples. The powder of the cured samples was put into boiling water for 3 h, and the thermal stability of the cured samples was investigated by TGA. Table V shows the results of the thermal stability of the cured samples before and after hydrolysis in N₂.

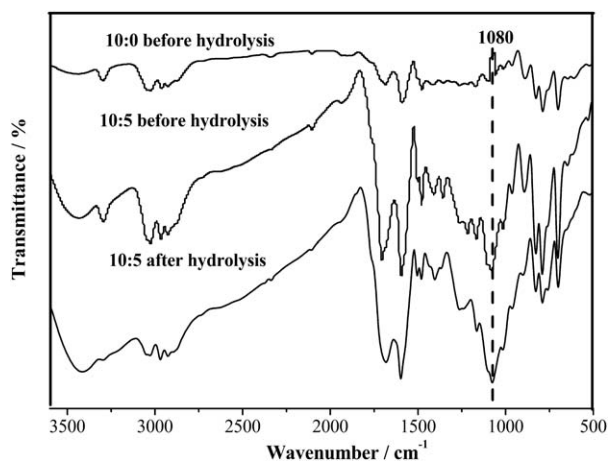


Figure 6. FTIR spectra of the cured samples (10:5 PAA/VTMS) before and after posthydrolysis.

From Table V, some conclusions could be drawn: (1) the char yield of the cured samples (PAA–VTMS) by posthydrolysis was higher than that of the cured samples (PAA–VTMS), with a relative value of 4.4% for the cured samples (10:5), and (2) the thermal decomposition temperature of the hydrolyzed PAA–VTMS was higher than that of the cured samples (PAA–VTMS), and for 10:5 PAA/VTMS, the thermal decomposition temperature of the hydrolyzed PAA–VTMS was elevated by 20°C.

Figure 6 presents the FTIR spectra of the cured samples (10:5 PAA/VTMS) before and after posthydrolysis. The absorption peak at 1080 cm^{-1} was attributed to the Si–O–C bonds before posthydrolysis. After posthydrolysis, it was hard to distinguish the peak of Si–O–Si from the peak of Si–O–C (the peaks may have overlapped). In the range 1000–1500 cm^{-1} , there were some differences between the cured samples before and after posthydrolysis that were due to the changes in the methoxy groups. At 3290 cm^{-1} , the hydrolyzed PAA–VTMS disappeared; this was associated with free terminal $\equiv\text{C}-\text{H}$ groups. From the FTIR results, we found that posthydrolysis was helpful

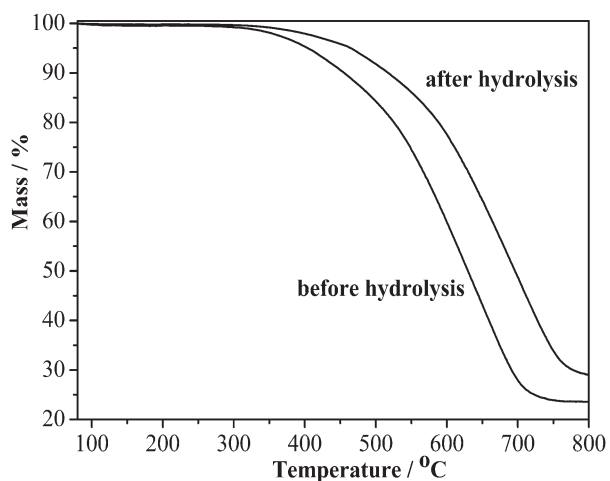


Figure 7. TGA profiles of the cured samples (10:5 PAA/VTMS) after hydrolysis in air.

for the elimination of the methoxy group and free terminal $\equiv\text{C}-\text{H}$ groups.

On the basis of the hydrolysis mechanism of silane, the methoxy groups were hydrolyzed to produce a Si–OH structure in boiling water, and the Si–OH groups produced by hydrolysis generated Si–O–Si bonds through a condensation reaction at elevated temperature; this increased the crosslinking density of the cured samples. With increasing content of VTMS, the proportion of Si–O–CH₃ groups was large; thus, the effect of hydrolysis on the thermal stability of the cured samples was more obvious.

Thermooxidative Stability of the Cured Samples that Were Hydrolyzed

Figure 7 shows the influence of posthydrolysis on the cured samples in air. After the cured samples were boiled, their heat resistance in air was better than that of the original cured samples, and the char yield in air grew from 23.5% (before hydrolysis) to 29% (after hydrolysis). Hydrolysis was also an effective way to improve the thermooxidative stability of the cured samples.

CONCLUSIONS

PAA modified by VTMS was successfully prepared from the blending of DEB and VTMS. SEM and FTIR investigations of PAA showed that VTMS copolymerized with DEB. TGA revealed that PAA modified by VTMS had a better thermooxidative stability than PAA. Through the application of postirradiation and posthydrolysis on the cured samples, the thermal stability in N₂ and air was greatly improved.

1. With increasing VTMS, the T_{d5} for the cured samples decreased from 430 to 402°C, and the residue yields at 800°C decreased from 79.5 to 75.8% in N₂, whereas the residue yields at 800°C increased from 12.5 to 23.6% in air.
2. After the cured samples (10:5 DEB/VTMS) were irradiated with a dose of 100 kGy, their T_{d5} in air was 461°C, and their char yield at 800°C in air was 26.3% (the char yield of PAA was 0% in air).
3. For the cured samples (10:5 DEB/VTMS), the char yield at 800°C in air was 23.5% before hydrolysis and 29% after hydrolysis.

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