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BIS(VINYLBENZYL) ETHER AND BIS(VINYLBENZYL) THIOETHER: SYNTHESIS, CURE STUDIES AND EVALUATION FOR COMPOSITES. Lon J. Mathias, Jeno Muthiah, Christopher C. Roberts. Department of Polymer Science, University of Southern Mississippi, Hattiesburg, MS 39406-0076. Bis(vinylbenzyl ether) and bis(vinylbenzyl thioether) have been synthesized from a meta/para mixture of vinylbenzyl chloride. Crude yields of greater than 90% were obtained for both VBE and VBT. The onset and peak temperatures for thermal cure (as observed by DSC) were 80°C/110°C, and 120°C/190°C, respectively. Both resins did not exhibit a T_g in the second DSC run due to high crosslink density. Crosslinking is assumed to take place through free radical polyaddition with high conversions achieved under thermal cure. Composites formed from these resin had flexural modulus values at room temperature comparable to, or better than, amine-cured epoxies. However, at temperatures above 200°C, the VBE and VBT materials had higher moduli than the epoxy samples while the loss in modulus values when heated to 250°C was much lower than for epoxy composites. In comparing VBT to VBE, it is clear that VBT composites gave a higher modulus to begin with, and maintained this difference up to 300°C. Above 350°C, however, the flexural modulus of VBT drops to 22% of its initial value, whereas VBE only dropped to 50%. This is due to faster decomposition of VBT at 350°C as confirmed by TGA. Overall, these new resins offer excellent promise for use in high performance composites.					
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**Bis(vinylbenzyl) Ether and Bis(vinylbenzyl) Thioether:
Synthesis, Cure Studies and Evaluation for Composites**
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Introduction

Vinylbenzyl (or styryl) terminated monomers are a new class of thermosetting resins which can be cured thermally with no evolution of volatiles. The cured resins have good thermal stability, excellent moisture resistance and low dielectric constant.¹ As shown earlier, vinylbenzyl groups can be cured neat or with added free radical initiator.² The onset temperature of the curing exotherm varies from 110°C to 180°C depending on the connecting group between the vinylbenzyl ether groups.³ A 4+2 cycloaddition process involving two styrene moieties has been proposed; this mechanism is analogous to that reported to occur in the bulk polymerization of styrene at 150°C in which dimerization of styrene was observed.⁴

This paper describes a single-step synthesis of the lowest members of this family, bis(vinylbenzyl) ether (VBE) and bis(vinylbenzyl) thioether (VBT), which were obtained from vinylbenzyl chloride. We are aware of only one reference mentioning VBE obtained from *p*-vinylbenzyl chloride.⁵ We have used FTIR, NMR, and DSC analysis along with DMA and 3-point bending tests to evaluate the curing temperatures, conversion under thermal cure, and physical properties for VBE and VBT composites. VBE-terminated resins have been used for laminates with glass roving to give material with a flexural modulus value of 7.9 GPa.³ These resins are excellent matrices for carbon fiber composites due to their high hydrocarbon content.

Experimental

Solvents and reactants were commercially available and used without further purification. A commercial sample of vinylbenzyl chloride (VBC) containing 30% *para*- and 70% *meta*- isomers was used as obtained from the Aldrich Chemical Co. AS-4 unsized carbon fibers were donated by Hercules Chemical Co. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR. ¹³C NMR spectra were obtained in CDCl₃ on Bruker AC-300 and AC-200 spectrometers. ¹³C CP/MAS spectra were obtained on a Bruker MSL-200 spectrometer. A DuPont 9900 data station and DSC, TGA and DMA modules were used for thermal characterization. Flexural moduli were also calculated from 3-point bending tests using an MTS-810 system with a span-to-thickness ratio of 16:1 and strain rate of 2 mm/min.

Synthesis of VBE and VBT

VBE was prepared and purified according to the procedure reported earlier.⁶ The following procedure was adopted for the synthesis of VBT. A mixture of 140 mL water, 0.4 g Aliquat 336, and 11 g Na₂S•9H₂O (0.046 mol) was stirred in a 250 mL round bottom flask. After purging with N₂, vinylbenzyl chloride (10 g, 0.066 mol) was mixed with the solution via a mechanical stirrer. The mixture was heated in a water bath to 60-70°C for 1.5 hrs under high speed mixing conditions. During this time, the mixture changed from an intense yellow to orange color. The mixture was allowed to react for an additional hour without heat, transferred to a separatory funnel using 200 mL hexanes rinse, and washed several times with water. The organic layer was rotary evaporated to yield VBT (96% by GC).

Composite samples (width = 13 mm, length = 65 mm) were prepared in a custom made steel mold. VBE samples were cured at 200°C for 10-12 hour, and VBT samples were cured at 165°C and 205°C for 5 hours at each temperature. The composites contained approximately 30% resin by weight after cure. A control sample with Epon-828/MDA as matrix material with carbon fibers was also prepared by heating 4h at 75°C and 2h at 175°C.

Results and Discussion

Ether synthesis

Figure 1 shows the synthesis of VBE and VBT plus the isomer ratios for the starting material and products. Yields of the ether were typically greater than 85-90%, and the compound was obtained crude in ca 90% purity by GC. VBT was obtained in ca 95% crude yield. Residual aliquat 336 was removed by chromatography on silica gel (50-200 mesh). VBT formation was confirmed by ¹³C NMR monitoring of loss of the chlorobenzyl peak at 45 ppm and growth of the thioether carbon peak at 35 ppm. Crude products were typically used directly in the reactions described below without removal of residual VBC.

Thermal cure results

Resins were scanned in the DSC at 10 deg/min under nitrogen. The onset and peak temperatures observed for neat VBE cure (scanned up to 300°C) were ca 80°C and 110°C with a heat of curing of 600 J/g. No T_g was observed in subsequent scans. NMR and FT-IR analysis showed that thermal curing of VBE occurs mostly through vinyl polymerization.⁶ VBT showed similar cure behavior with heat of curing of ca 400 J/g, and onset and peak temperatures of approximately 120°C and 190°C, respectively. The thermogram showed two exotherm peaks, probably due to initial crosslinking leading to formation of a network with a T_g of ca 160-180°C followed by further cure above this temperature. A second DSC scan exhibited no transitions up to degradation at ca 350°C. ¹³C CP/MAS (Figure 2) of cured VBT showed only traces of residual vinyl carbons at 114 ppm similar to what was observed for cured VBE.⁶

Mechanical Testing Results

Dynamic Mechanical analyses were carried out at 4°C/min. In the first DMA run (to 250°C), the VBT resin gave the highest modulus of the three systems. Table 1 gives modulus values at different temperatures plus the temperature of tan δ_{max}. The tan δ_{max} appears at higher temperatures for VBE and VBT than for the epoxy samples. More importantly, about 87% of the initial moduli were maintained at 200°C for both VBE and VBT composites compared to only 28% for epoxy composites. The flexural modulus and strength calculated using 3-point bending test were 46 GPa and 308 MPa for the VBE samples and 75 GPa and 490 MPa for VBT samples.

Figure 3 shows the second-run DMA plots of the samples that were taken up to 250°C and cooled down to room temperature. The reduction in room temperature properties (after cooling) was highest for the epoxy samples, intermediate for VBT materials, and least for VBE composites. Table 2 gives the second-run modulus values at different temperatures and temperature corresponding to tan δ_{max}. The overall performance of VBT composites is better than VBE composites up to 300°C in the second run also. VBT composites maintained 80% of their room temperature moduli at 300°C whereas the VBE samples showed a 40% drop. At 350°C, the flexural moduli of VBT composites dropped to 22% of initial values whereas the drop for VBE composites was only 50%. This shows that even though the VBT resin has higher modulus up to 300°C and a higher tan δ_{max} temperature, decomposition begins at lower temperatures than for VBE composites.

The TGA curves for VBE and VBT are given in Figure 4. Both resins showed a weight loss of 4-5% at 350°C, while between 350 and 375°C, VBT lost 11% and VBE showed only a 7.5% weight loss. The same trend was noticed in the DMA results with 80% and 50% loss in modulus values for VBT and VBE composites, respectively, over the same temperature range.

Conclusions

Bis(vinylbenzyl ether) and bis(vinylbenzyl thioether) has been synthesized from a *meta/para* mixture of vinylbenzyl chloride. Crude yields of greater than 90% were obtained for both VBE and VBT. The onset and peak temperatures for thermal cure (as observed by DSC) were 80°C/110°C, and 120°C/190°C, respectively. Both resins did not



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exhibit a T_g in the second DSC run due to high crosslink density. Crosslinking is assumed to take place through free radical polyaddition with high conversions achieved under thermal cure. Composites formed from these resin had flexural modulus values at room temperature comparable to, or better than, amine-cured epoxies. However, at temperatures above 200°C, the VBE and VBT materials had higher moduli than the epoxy samples while the loss in modulus values when heated to 250°C was much higher for epoxy composites. In comparing VBT to VBE, it is clear that VBT composites gave a higher modulus to begin with, and maintained this up to 300°C. Above 350°C, however, the flexural modulus of VBT drops to 22% of its initial value, whereas VBE only dropped to 50%. This is due to faster decomposition of VBT at 350°C as confirmed by TGA. Overall, these new resins offer excellent promise for use in high performance composites.

References

1. Z. K. Liao and C. S. Wang, *Polym. Bull.*, 22, 1 (1989).
2. S. J. Barton, J. S. Ghotra, A. E. Mathews, and G. Pritchard, *J. Appl. Polym. Sci.*, 42, 35 (1991).
3. J. J. Zupanic, A. M. Zweig, J. P. Conrad, and E. A. Dinkel, *Prepr. ACS Div. Polym. Mat. Sci. Engin.*, 60, 610 (1989).
4. F. R. Mayo, *J. Am. Chem. Soc.*, 90, 1289 (1968).
5. J. Nishimura, D. Tomisaki, M. Ohta, S. Yamashita in "Cyclopolymerization and Polymers with Chain-Ring Structures," George B. Butler and Jiri E. Kresta, Eds., American Chemical Society, Washington, 1982, p 190.
6. J. Muthiah, L. J. Mathias, *J. Polym. Sci. Part A, Polym. Chem.*, 30, 509 (1992).

Table 1. DMA Results (First Run) for Carbon Fiber Composites.

Resin	Flexural Modulus in GPa at				tan δ_{max} (°C)
	50°C	100°C	150°C	200°C	
VBT	47.25	46.24	44.28	41.10	220
VBE	33.83	33.37	32.57	29.50	242
Epon-828/MDA	40.12	38.07	35.33	11.30	200

Table 2. DMA Results (Second Run) for Same Carbon Fiber Composites (Above).

Resin	Flexural Modulus in GPa at					tan δ_{max} (°C)
	100°C	200°C	250°C	300°C	350°C	
VBT	37.42	34.61	32.46	30.11	8.39	270
VBE	31.77	28.04	23.54	19.73	16.56	248
Epon 828/MDA	22.19	10.26	2.833	-	-	220

PVP

Figure 1. Synthesis of VBE and VBT

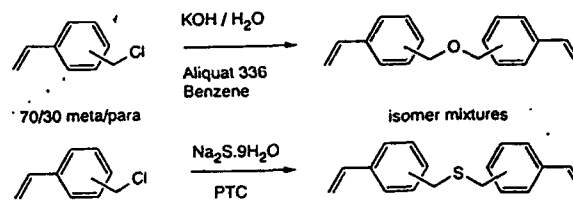


Figure 2. ^{13}C NMR spectra of VBT neat resin (bottom) and VBT cured at 165°C (5hrs) and 205°C (5hrs) (top)

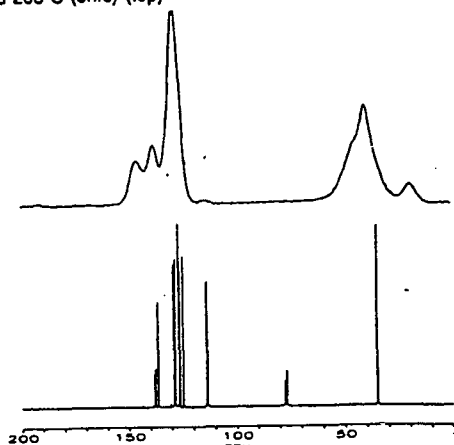


Figure 3. DMA analysis of carbon fiber composites of VBT (—), VBE (---) and epoxy (---) at 4°C/min after first run to 300°C.

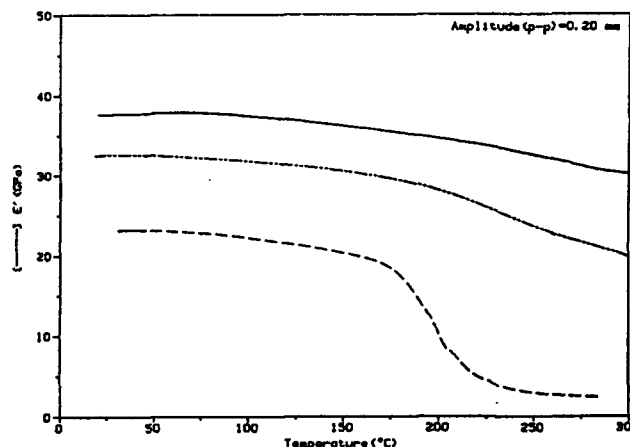
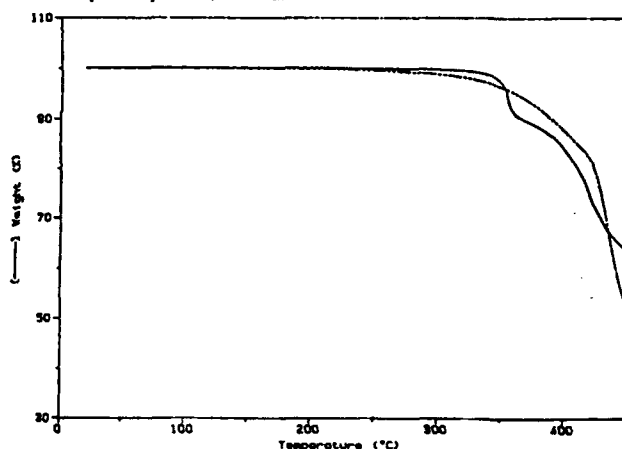


Figure 4. TGA analysis of VBT cured at 205°C (—) and VBE cured at 200°C (---) at 10°C/min in air.



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