Novel vinyl ether thermosetting resins*

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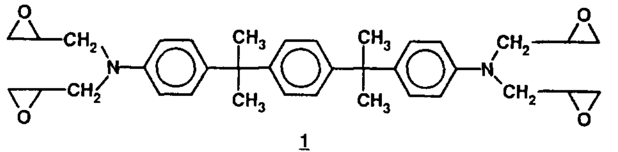
The divinyl ether of diallylbisphenol A (VEABA) was investigated as a candidate for advanced composite matrix resin. VEABA was readily prepared in over 90% yield from a condensation reaction between diallyl bisphenol A and chloroethyl vinyl ether using a phase transfer catalyst. Since vinyl ethers are electron-rich monomers, they are polymerized by cationic initiators. The VEABA polymer possesses properties comparable to polymers produced from epoxy resins based on the diglycidyl ether of bisphenol A, except for much lower moisture absorption and a slightly lower glass transition temperature. Since the VEABA monomer is a low viscosity liquid, it is a good candidate for filament winding, resin transfer moulding and pultrusion fabrications for advanced composites.

(Keywords: thermosetting resins; composite matrix; vinyl ether)

INTRODUCTION

Epoxy resins are widely used as matrix resins for advanced composites in aerospace/aircraft and electric/electronic applications. Advanced composites fabricated from epoxy resins based on the diglycidyl ether of bisphenol A (DGEBPA), or its derivatives, possess excellent physical properties, such as good adhesion, excellent chemical resistance and good dimensional stability.

One drawback of the DGEBPA-based epoxy resins, however, is high moisture absorption, causing poor hot and wet properties. Thus, several new epoxy resins and epoxy curing agents have been developed to reduce moisture absorption by incorporating sterically hindered epoxy groups and/or bulky hydrophobic moieties. For example, tetrafunctional epoxy resins, *1*, and diglycidyl-9,9′-bis(4-hydroxyphenyl)fluorene) epoxy resins, *2*, were developed for high performance advanced composite and adhesive applications[1]. Bulky, hydrophobic dicyclopentadiene backbone epoxy resins, *3*, were also developed and they absorb less moisture while maintaining good physical properties at a 150°C service temperature[2].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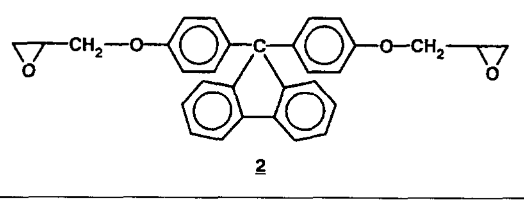
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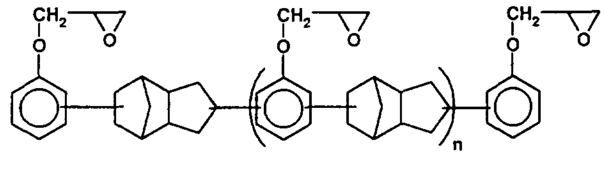
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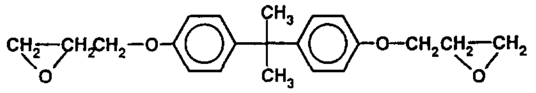
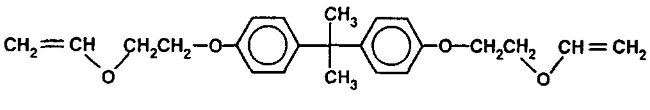
Besides those epoxy resins, cyanate ester and bismaleimide resins are widely used for high temperature advanced composite applications[3,4]. Vinyl ethers were also reported to be candidates for composite matrix resins and the divinyl ether of bisphenol A (DVEBPA) was prepared from the reaction between bisphenol A and chloroethyl vinyl ether[5].

DVEBPA possesses a structure similar to that of DGEBPA and the physical properties of their resulting polymers are indeed comparable, as shown in *Table 1*. However, DVEBPA monomer is a solid with a m.p. of 55°C. Thus, it requires heating or it must be dissolved in reactive diluents for resin transfer moulding and filament winding applications.


DGEBPA


DVEBPA

This paper discusses the development of an aromatic divinyl ether with low viscosity for filament winding, resin transfer moulding and pultrusion applications.

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Table 1 Physical properties of DVEBPA and DGEBPA polymers

	DVEBPA	DGEBPA
Flexural modulus (MPa)	2800	2940–3080
Heat distortion temperature (°C)	168	170–182
T_g (°C)	139	137

EXPERIMENTAL

Monomer synthesis

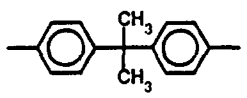
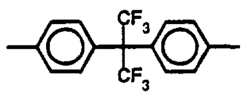
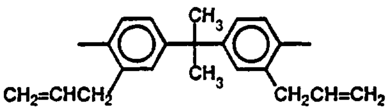
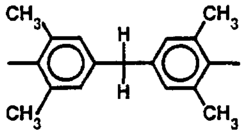
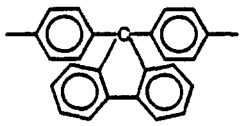
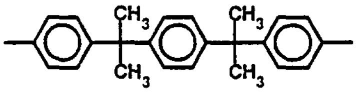
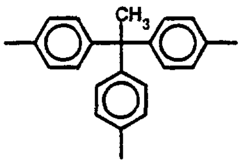
The divinyl ether of diallyl bisphenol A (VEABA), a novel liquid vinyl ether resin, was readily prepared from the reaction of chloroethyl vinyl ether and diallyl bisphenol A, either in heptane solution with a phase transfer catalyst or in dimethylsulfoxide (DMSO) solvent (*Scheme 1*).

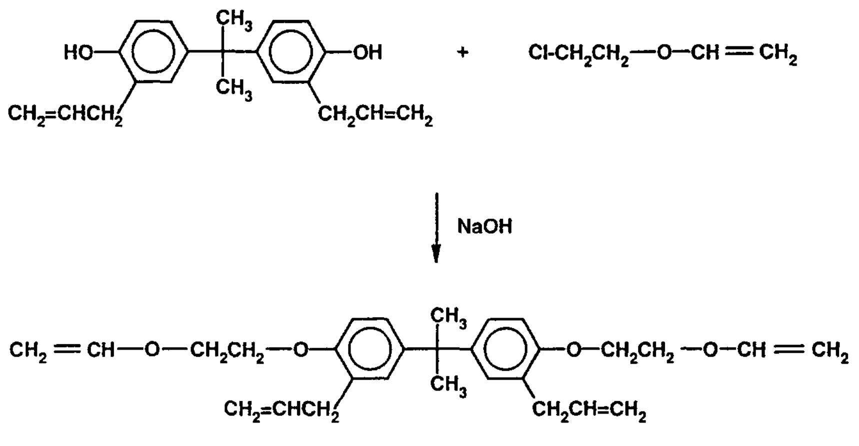
All starting materials were used as received without further purification. Diallyl bisphenol A (DABPA) (61.6 g, 0.2 mol), tetrabutylammonium bromide (0.46 g, 0.0014 mol), chloroethyl vinyl ether (144 g, 1.4 mol), and heptane (50 ml) were charged to a 500 ml four-necked flask equipped with a mechanical stirrer, a condenser, a thermometer and a nitrogen inlet. This mixture was stirred for 10 min at room temperature, or until all of the DABPA had dissolved. Sodium hydroxide (18 g, 0.45 mol) was added and the mixture was heated to 80°C and stirred for 3 h. When the reaction was complete, the reaction mixture was cooled and 200 ml of water was added to dissolve sodium chloride. After removing the aqueous layer, the organic layer was washed with 100 ml of saturated NaCl solution and with 100 ml of water. The organic layer was dried over $MgSO_4$ and filtered. It was then stirred for 15 min with 10 g of acidic alumina and filtered. Solvent was removed under reduced pressure. The product was vacuum dried for 1 h at 50°C and 1 mmHg and isolated in a yield of 81.5 g (91%).

The advantages of using a phase transfer catalyst are higher yield (90% compared to 70%), easier removal of heptane solvent relative to DMSO, simple reaction analysis by h.p.l.c., and a less coloured product compared to that prepared in DMSO solution. As shown in *Figure 1*, the optimum level of tetrabutylammonium bromide phase transfer catalyst is approximately 7 wt%.

Besides VEABA, other aromatic divinyl ethers, *4–10*, were also prepared in generally good yield using the identical synthetic method to that for VEABA, as shown in *Table 2*. In addition to VEABA, *6*, divinyl ethers *7* and *8* are low viscosity pourable liquids while the remaining divinyl ethers are crystalline solids.

Table 2 Yields and melting points of various divinyl ethers $CH_2{=}CH\text{-}O\text{-}CH_2CH_2O\text{-}R\text{-}OCH_2CH_2\text{-}O\text{-}CH{=}CH_2$

R		Yield (%)	Melting point (°C)
	*4*	94	55
	*5*	95	109
	*6*	91	liquid
	*7*	85	liquid
	*8*	60	liquid
	*9*	90	98
	*10*	60	103



VEABA

Scheme 1

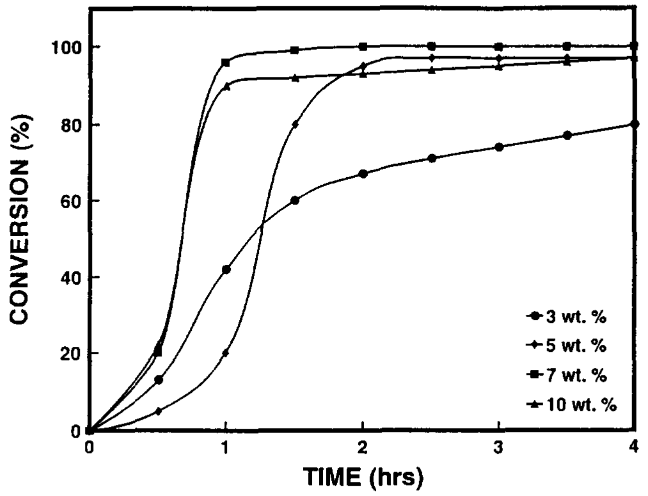


Figure 1 Effect of phase transfer catalyst level on the monomer conversion

Formulation stability

Since vinyl ethers are electron-rich monomers, they polymerize readily at room temperature with cationic initiators or under u.v. irradiation using u.v. cationic photoinitiators[6,7].

VEABA monomer was formulated with 1 wt% of triarylsulfonium hexafluoroantimonate u.v. cationic initiator, and 10 g of this mixture was stored in a glass vial at ambient temperature and at 50°C. The viscosity was measured on a Brookfield cone and plate viscometer at intervals of 1 month.

Polymer film preparation

Polymer films were prepared for physical property and electrical property evaluation by placing the formulation between two glass slides with dimensions 15 cm x 15 cm with a polyethylene liner and a 0.75 mm Teflon spacer. To VEABA and cycloaliphatic epoxy, *11*, was added 1 wt% of triarylsulfonium hexafluoroantimonate initiator, and the formulations were cured for 20 s per side under 30 mW cm^{-2} of u.v. intensity. The polymer films were post-cured at ambient temperature for a minimum of 24 h before testing.

Measurements

Differential photocalorimetry (d.p.c.) measurements were obtained on a TA Instrument 930 differential photocalorimeter, equipped with a TA Instrument thermal analyst 2100. Glass transition temperatures, T_gs, were obtained by dynamic mechanical analysis (d.m.a.) on a Rheometrics dynamic analyser RDA II. Decomposition temperatures were determined by thermogravimetric analysis (t.g.a.) on a TA Instrument 951 thermogravimetric analyser.

The test methods used for measuring physical and electrical properties were as follows:

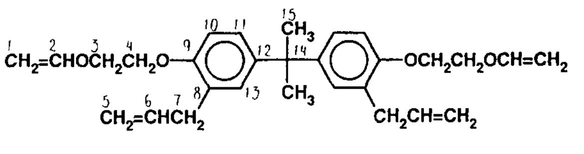
Tensile strength	ASTM D-882
Modulus	ASTM D-882
Elongation	ASTM D-882
Shrinkage	STM 641
Moisture absorption	ASTM D-570
Dielectric constants	ASTM D-150
Dissipation factors	ASTM D-150
Dielectric strength	ASTM D-149

RESULTS AND DISCUSSION

Monomer

The structure of VEABA was confirmed by i.r., ^{1}H and ^{13}C n.m.r. spectroscopy. The i.r. spectrum showed vinyl ether absorptions at 1617 and 1637 cm^{-1}, and the ^{1}H n.m.r. spectrum is shown in *Figure 2*.

The ^{13}C n.m.r. spectrum is shown in *Figure 3* and the carbon assignments are as follows:



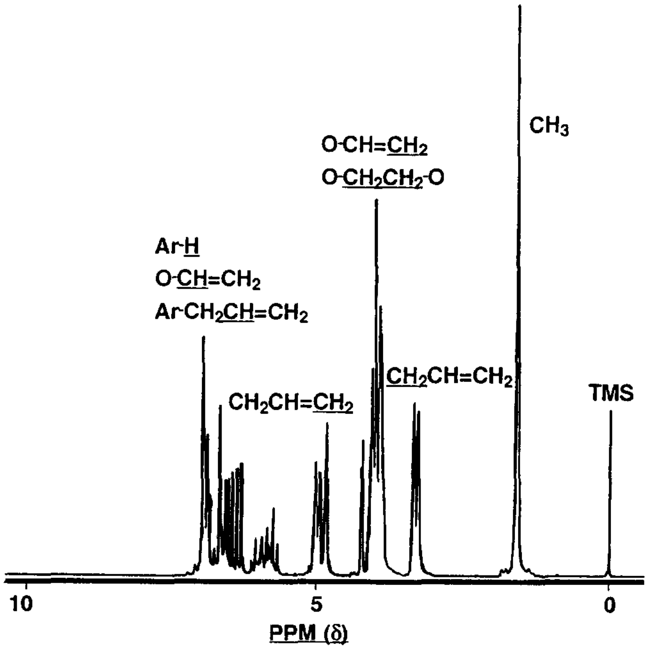


Figure 2 ^{1}H n.m.r. spectrum of VEABA

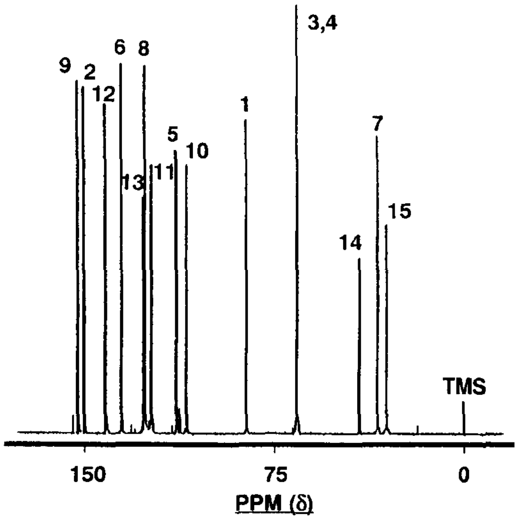


Figure 3 ^{13}C n.m.r. spectrum of VEABA

Carbon	ppm (γ)	Carbon	ppm (γ)
1	86.9	8	128.1
2	151.7	9	154.1
3	66.7	10	111.0
4	66.7	11	125.3
5	115.1	12	143.3
6	137.1	13	128.4
7	34.6	14	41.6
		15	31.0

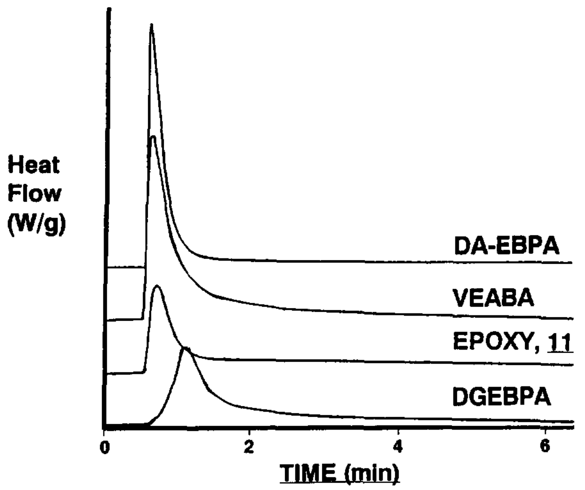


Figure 4 Differential photocalorimetry of various u.v. curable monomers

Table 3 Viscosity of VEABA formulation over time

	Viscosity (cps)	
Time (months)	at ambient temperature	at 50°C
0	290	290
1	–	310
2	295	305
3	290	290
6	290	540

Polymerization

As shown in *Figure 4*, a d.p.c. study clearly indicates that the polymerization speed of VEABA monomer under u.v. irradiation is much faster than that of the most widely used u.v. curable cycloaliphatic epoxy monomer, 3,4-epoxy cyclohexylmethyl-3,4-epoxy-cyclohexane carboxylate, *11*, and DGEBPA. The u.v. initiated polymerization speed of VEABA is almost as fast as that of a free radically polymerizable monomer, the diacrylate of ethoxylated bisphenol A (DA-EBPA).

Despite the high reactivity of the vinyl ether monomer, the monomer formulated with 1 wt% of a triarylsulfonium hexafluroroantimonate u.v. cationic photoinitiator is so stable that the viscosity remained unchanged over 6 months at ambient temperature, as shown in *Table 3*. Even at an elevated temperature of 50°C, the formulation viscosity remained stable over 3 months.

Polymer physical properties

The physical properties of the respective polymers are shown in *Table 4*. Most of the physical properties of the VEABA polymer are comparable to those of the DGEBPA polymer. The VEABA polymer did not absorb a measurable amount of water, while the DGEBPA polymer absorbed 1.1% water under the same conditions.

Electrical properties of the VEABA and cycloaliphatic epoxy, *11*, polymers are summarized in *Table 5*. Overall, the electrical properties of the VEABA polymer are superior to those of the cycloaliphatic epoxy polymer, *11*, probably due to the lack of free hydroxyl groups in the polymer chains.

The VEABA polymer is quite stable and t.g.a. shows the polymer decomposition temperature to be 375–400°C.

Table 4 Physical properties of VEABA and DGEBPA polymers

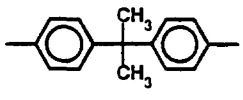
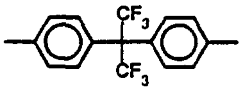
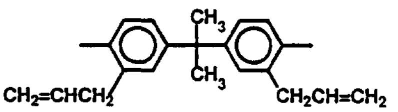
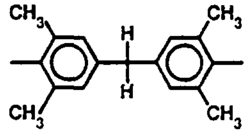
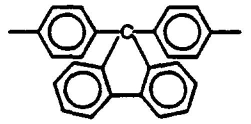
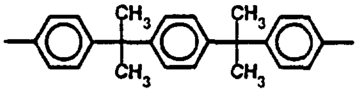
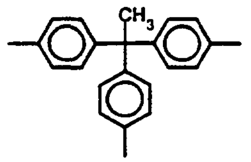
Physical property	VEABA	DGEBPA
Tensile strength (MPa)	41.3	34.3
Elongation (%)	2.7	1.3
Modulus (MPa)	2100	3157
Shore D	80	82
Shrinkage (%)	6.3	4.0
Moisture absorption (%)	nil	1.1

Table 5 Electrical properties of vinyl ether and epoxy polymers

Electrical property (1 kHz)	VEABA	Cycloaliphatic epoxy, *11*
Dielectric constant	3.2	3.5
Dissipation factor	0.012	0.017
Dielectric strength	1035	838

Table 6 Glass transition temperatures of various divinyl ether polymers

$CH_2{=}CH\text{-}O\text{-}CH_2CH_2O\text{-}R\text{-}OCH_2CH_2\text{-}O\text{-}CH{=}CH_2$

R		T_g (°C)
	*4*	134
	*5*	143
	*6*	81
	*7*	117
	*8*	–
	*9*	118
	*10*	110

The T_gs of the aromatic divinyl ether polymers are summarized in *Table 6*. The T_g of VEABA is slightly lower than that of DGEBDA epoxy resin and DVEBPA ether, *4*, probably due to the presence of allyl groups in the

BPA moiety. However, the T_g of VEABA could be increased by copolymerization with an electron-deficient monomer, such as a bismaleimide. High heat distortion temperatures, above 200°C, are reported by copolymerizing electron-rich DVEBPA and electron deficient *N,N'*-4,4'-diphenylmethyl bismaleimide at elevated temperatures[8].

Even higher heat distortion temperatures might be obtained when VEABA is used instead of DVEBPA. An allyl group on VEABA could initially participate in an ene reaction with one maleimide, and this product could subsequently react with a second maleimide in a Diels–Alder reaction, as shown in *Figure 5*[9].

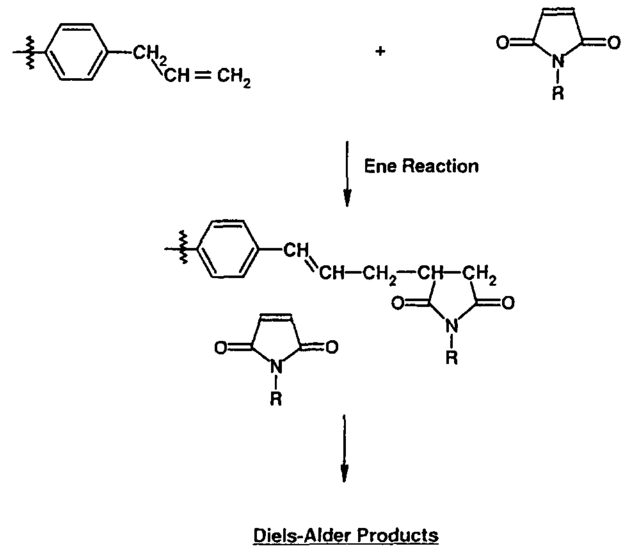


Figure 5 Diels–Alder reaction between a maleimide and the ene reaction product

CONCLUSIONS

New aromatic divinyl ethers were prepared in good yield. They are readily polymerized under u.v. light in the presence of a u.v. cationic photoinitiator to produce polymers with physical and electrical properties comparable to those of epoxy resins. Other advantages include low shrinkage, low moisture absorption and low toxicity. Thus, the liquid and low melting point vinyl ethers could be matrix resin candidates for resin transport moulding and filament winding applications.

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