



Studies on flame retardant vinyl ester resin

Patel R.H. * and Sevkani V.R.

Department of Materials Science, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India
rasmi29@yahoo.com

Available online at: www.isca.in, www.isca.me

Received 3rd December 2016, revised 24th January 2017, accepted 10th February 2017

Abstract

Vinyl ester resins are widely used for coating purpose and well known for their excellent anti-corrosive, anti-oxidative properties. Traditional vinyl-esters are generally synthesized by reacting unsaturated monocarboxylic acid with epoxy in resinous form in the presence of tertiary amines as a catalyst. In the present work a flame-retardant vinyl ester resin has been prepared by reacting epoxy resin based on Tris m-hydroxy phenyl phosphate (THPP) with methacrylic acid in presence of triethyl amine as catalyst and hydroquinone as an inhibitor. This polymer was characterized by chemical analysis, elemental analysis, FTIR and NMR Spectroscopy (¹H, ¹³C and ³¹P). This vinyl ester was further reacted with styrene in presence of an initiator for certain time period. The resultant polymer was used for coating purpose in neat form as well as in the form of blend with epoxy resin. Various coating properties like hardness, adhesion, flexibility, chemical resistancy of the coated panels have been found out. The polymer shows flame-retardancy as well as good scratch hardness and chemical resistance properties.

Keywords: Flame-Retardant, Vinyl ester, Analysis, Coating, Properties.

Introduction

Vinyl ester resins are mainly synthesized by reaction of epoxy resin (DGEBA) with several types of unsaturated acids such as acrylic acid, methacrylic acid, crotonic acid, etc. In the present work phosphorous based flame retardant vinyl ester resin having anti-corrosive properties has been synthesized. First phosphorous based epoxy resin was prepared from tris m-hydroxy phenyl phosphate, which was allowed to react with methacrylic acid to get vinyl ester resin. Blending was carried out with different proportions of styrene. The resultant polymer was mixed with different proportions of conventional epoxy resin, which were ultimately used for casting films and coating purposes. Resins and blends were characterized by various methods like FTIR, NMR, GPC, TGA and DSC. Coated panels were tested by scratch hardness, pencil hardness and adhesion test. Films were used to test flame retardant properties like LOI (limiting oxygen index) and UL (Underwriter laboratory)-94. Coated panels were stable in continuous exposure in alkali medium and acidic medium for 19-35 days.

Experimental: The experimental part is divided in three parts i. Synthesis of tris m-hydroxy phenyl phosphate ii. Synthesis of diglycidial ether of tris m-hydroxy phenyl phosphate iii. Synthesis of vinyl ester resin.

Materials and methods

Resorcinol, phosphorous oxychloride, N,N-dimethylaniline, methacrylic acid, triethyl amine, styrene, benzoyl peroxide, and diethylene triamine all were procured from Merck chemicals, Germany. Epoxy resin was obtained from Atul limited, valsad.

Synthesis of tris m-hydroxy phenyl phosphate (THPP):

THPP was prepared as the method reported in the literature^{1,2}. Resorcinol and phosphorous oxychloride in the ratio 3:1 were heated in presence of N,N-dimethyl aniline as a catalyst around 110°C-115°C for 3.5hrs. After crystallization a pure product was obtained having melting point 210°C-213°C.

Synthesis of Diglycidyl ether of tris m-hydroxyl phenyl phosphate (DGETHPP):

One mole of THPP was allowed to react with two moles of epichlorohydrin in the presence of 10% NaOH solution at 120°C in an oil bath under continuous stirring for 5 hours. After completion of reaction vacuum distillation was carried out to remove excess epichlorohydrin. Epoxy equivalent weight was determined by dioxane in HCl method and was 325 gm/equivalent. Hydroxyl value of epoxy was determined by hydroxy equivalent weight and it was 1.89.

Synthesis of vinyl-ester resin: One mole of DGETHPP was reacted with 2 moles of methacrylic acid in presence of triethyl amine (0.1% w/w) and hydroquinone (0.1%w/w) at 100°C in an oil bath for 5-6 hours. Acid value was measured throughout the reaction and when it reached to 62 mg/KOH reaction was stopped^{3,4}.

Reaction scheme of vinyl-ester resin is shown in scheme-1.

Blending of Vinyl Ester Resin Vinyl ester resin was then mixed with a reactive diluent styrene in different amount i.e. 45%w/w, 40% w/w, 35% w/w in presence of benzoyl peroxide (2%w/w) to prepare vinyl ester blend. The vinyl ester blends have very poor film forming properties. To obtain suitable films these blends were then mixed with a conventional diglycidyl ether of

bisphenol A(DGEBA) resin in different proportions. Mixing with DGEBA resulted in films with better mechanical properties.

hours and in oven at 70°C for 4-9 hours for post-curing. Curing and post curing time required for vinyl ester blends are shown in Table-1.

Casting of the films were done in the glass mould (5cms length×5cms width×1.5 cm thickness) at room temperature for 16-22

Table-1 shows that System-3 required minimum time for curing and post curing.

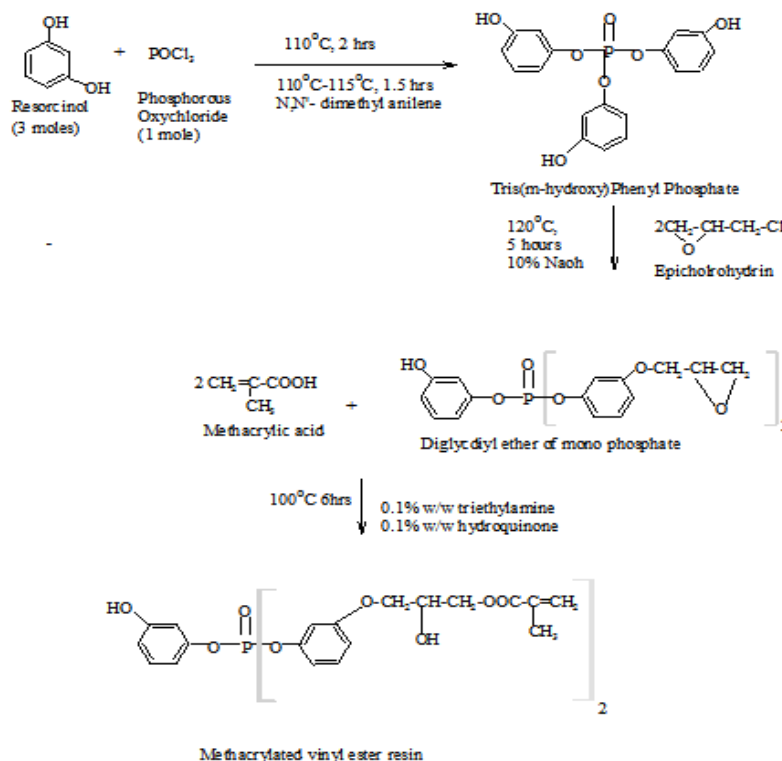


Table-1: Curing time and post-curing time of the vinyl ester blends.

Sr. No.	System	Blending Ratio (DGEBA: Vinyl ester resin)	Curing time (Room Temperature) (Hours)	Post-Curing time (70°C) (Hours)
1	System-1 (35%w/w) (Styrene)	90:10	16	7
		80:20	18	8
		70:30	21	9
2	System-2 (40%w/w) (Styrene)	90:10	19	6
		80:20	21	7
		70:30	22	7.5
3	System-3 (45%w/w) (Styrene)	90:10	17	4
		80:20	19	4.5
		70:30	20	5

Blended resins were coated on mild steel panels with the help of film applicator. Coated panels were kept at room temperature for 24 hours as well as in oven at 70°C for 12 hours. Different properties of panels were measured like scratch-hardness, adhesive properties, chemical resistance and pencil hardness.

Characterizations: The prepared vinyl ester resin was characterized by various methods as like Fourier Transformer Infrared (FTIR) Spectroscopy to determine functional groups of vinyl ester by perkin elmer instrument Model SPECTRUM GX, FT-IR spectrophotometer, Gel permeation chromatography (GPC) to determine average molecular weight of resin by perkin elmer instrument Model Series 200, Nuclear magnetic resonance(NMR) to study the types of protons, carbons and phosphorous by bruker 400MHz, Switzerland. Thermal gravimetric analysis to study the weight loss of resin by perkin elmer instrument TGA-7 and Differential scanning calorimetry PerkinElmer Pyris1 DSC to find out curing temperature of prepared resins. Flame-Retardancy of the films was checked by Limiting Oxygen Index and Underwriter Laboratory-94 method.

Results and discussion

FTIR: Vinyl ester resin was characterized by FTIR. The band at 3428 cm⁻¹ shows presence of free hydroxyl group. Peak at 2926 cm⁻¹ shows the presence of carboxylic group, sharp peak at

1727 cm⁻¹ shows presence of C=O stretch, peak at 1243 cm⁻¹ shows P-O-P stretch and peak at 1094 cm⁻¹ shows that P=O bond.

GPC: GPC was done in tetrahydrofuran as solvent for epoxy and vinyl ester resin. For, Epoxy resin Polymer dispersity index (PDI) value is 1.464 and number average molecular weight is 538. For, vinyl-ester resin Polymer dispersity index value (PDI) is 4.352 and number average molecular weight is 725.

NMR: ¹H, ¹³C and ³¹P NMR spectra of vinyl-ester resin were obtained by Bruker 400MHz using acetone solvent and tetra methyl silane as a reference solvent. From ¹H NMR sharp singlet at δ 3.01ppm and at δ 1.15 ppm are due to the presence of hydroxyl group and the presence of methyl group attached on the hydrogen, from ¹³C NMR singlet at δ30.14 ppm is due to the presence of oxygen at both terminal carbons and phenyl pendant hydroxyl group is present in the phenyl ring. From ³¹P NMR a peak at δ -12.75 ppm due to presence of P=O in compound and attachment of free hydroxyl group a small peak at δ 18.10 ppm is observed.

TGA: Thermal Gravimetry Analysis was done to find out weight loss with respect to temperature of three different systems. Results are shown in Table-2.

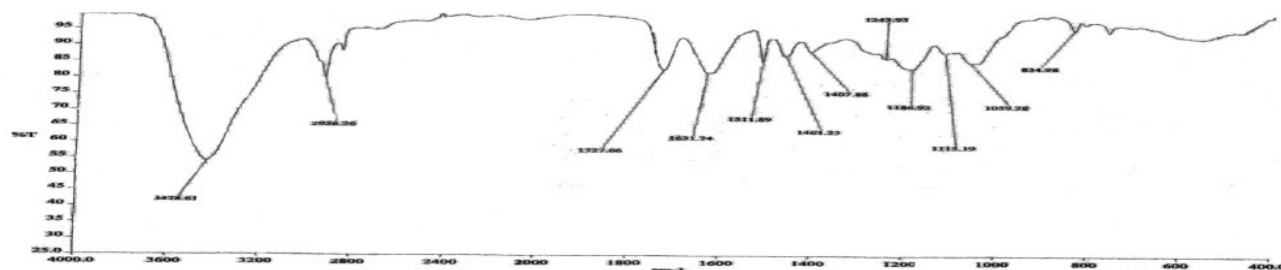


Figure-1: FTIR of Vinyl ester resin.

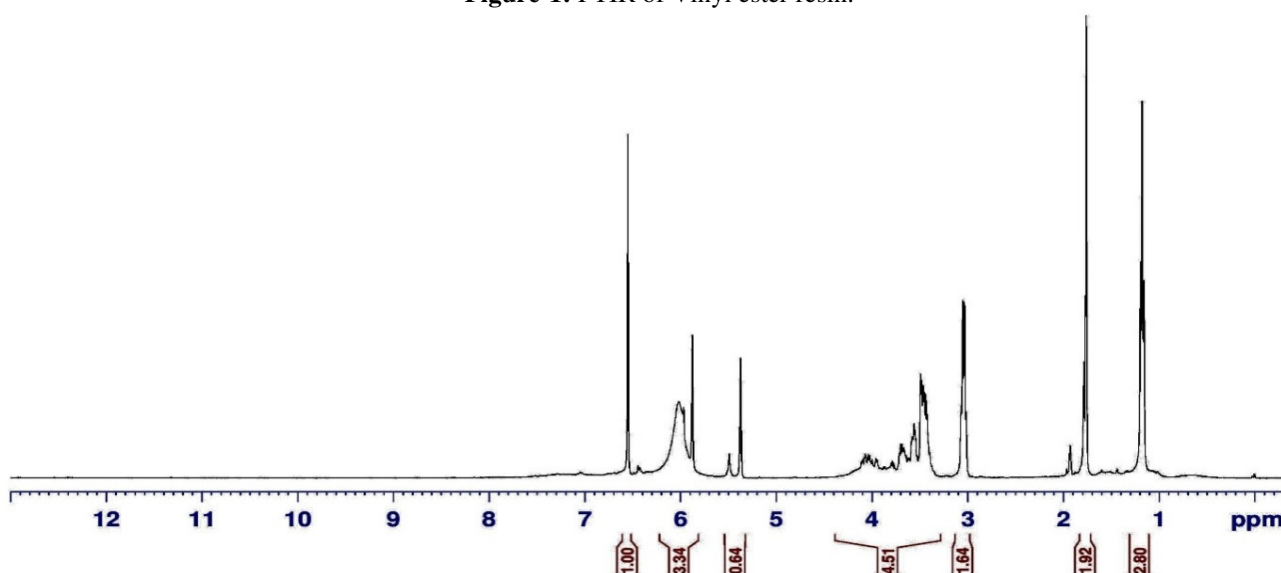


Figure-2: Proton NMR.

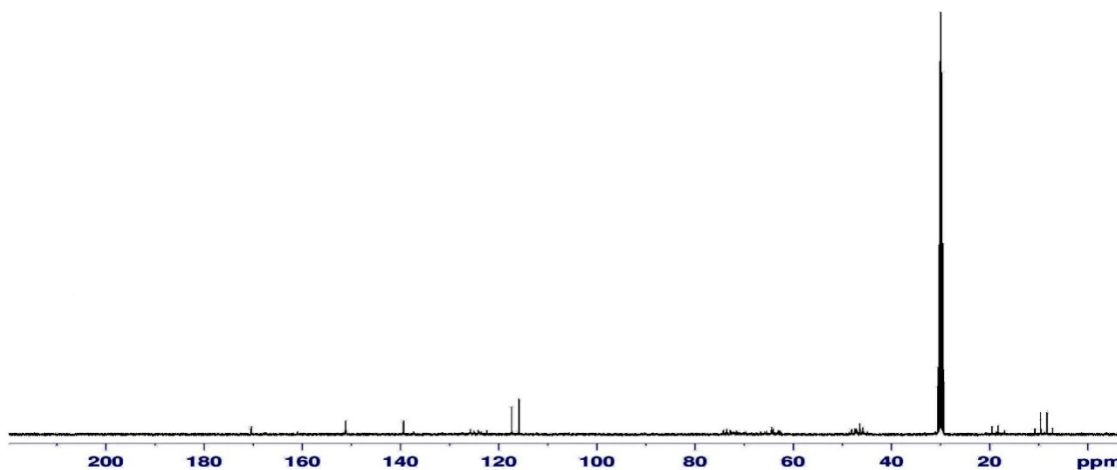


Figure-3: Carbon NMR.

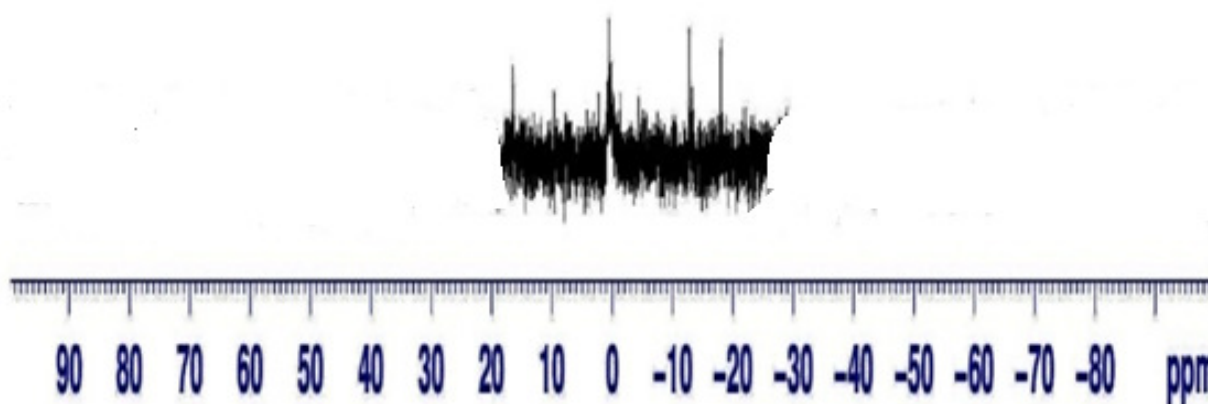


Figure-4: Phosphorous NMR.

Table-2: TGA data weight loss at different temperatures and char yield at 400°C.

Sr.No.	System	Blending Ratio (DGEBA: Vinyl ester resin)	Weight Loss in air(%)Temperature(°C)			Char Yield at 400°C (%)
			10%	20%	30%	
1	System-1 (35%W/W) (Styrene)	90:10	300	330	350	22.4
		80:20	250	300	350	20.9
		70:30	150	250	300	15.5
2	System-2 (40%W/W) (Styrene)	90:10	200	250	300	19.3
		80:20	200	300	310	22.4
		70:30	200	300	320	19.9
3	System-3 (45%W/W) (Styrene)	90:10	310	335	350	25.7
		80:20	300	350	370	35.3
		70:30	200	300	380	27.3

Table-2 shows that system-3 has maximum char yield 35% at 400°C. System-3 has good stability among all the systems.

DSC: For obtaining curing temperature and energy released values, Differential Scanning Calorimetric technique was used. Results are shown in Table-3.

Table-3 shows that system-3(90:10) has maximum curing temperature of 76.2°C and (70:30) has minimum peak temperature 62.5°C.

Coating: Resultant vinyl ester blends were coated on mild steel panels which was subjected to different hardness analysis such as scratch hardness, pencil hardness, adhesion properties and corrosion resistance in different acidic and alkali medium^{3,4}.

Table-4 shows that system 3 has maximum value of different hardness tests, corrosion resistance and good adhesion properties.

Flame-Retardancy: LOI: The test specimen was clamped vertically in the center of a column and ignited from the top in an known atmosphere nitrogen/oxygen mixture with a fixed flow rate. The concentration of oxygen was adjusted to meet the criteria of length or time of burning of test specimen.

UL-94: The standard test specimen (25 mm width × 450 mm length) was suspended vertically and exposed to a flame of burner at its lower end. Time of burning is measured. If the specimen burns upto the gauge mark, the rate of burning was measured but when it extinguished earlier, the time and extent of burning is measured. For flexible plastic film, the specimen is clamped at 45° angle. When the sample is removed from the flame, it must stop burning within ten second and there should not be any drippings of burnt or molten resin^{6,7}. In this case the film achieves V-0 rating. If the film continues to burn or if drips resin, V-1 or V-2.

Table-3: DSC data and energy released of prepared blends.

Sr. No.	System	Blending Ratio (DGEBA: Vinyl ester resin)	Curing Temperature (°C)	Energy Released (J/g)
1	System-1 (35%W/W) (Styrene)	90:10	66.1	9.8
		80:20	67.3	4.3
		70:30	62.5	4.8
2	System-2 (40%W/W) (Styrene)	90:10	63.7	11.6
		80:20	65.6	3.5
		70:30	70.3	3.1
3	System-3 (45%W/W) (Styrene)	90:10	76.2	3.4
		80:20	67.0	7.4
		70:30	62.5	5.8

Table-4: Coating properties.

Sr No.	System	Blending ratio (DGEBA :Vinyl ester resin)	Scratch Hadness gms	Pencil hardness	Adhesion (Cross-hetch)	Chemical resistance in days		
						10 % NaOH solution	10% HCl solution	10% H ₂ SO ₄ solution
1	System-1 (35%W/W) (Styrene)	90:10	400	1H	F	25	20	21
		80:20	430	H	P	21	17	18
		70:30	450	2H	P	22	25	27
2	System-2 (40%W/W) (Styrene)	90:10	510	2H	F	25	20	21
		80:20	530	3H	P	21	17	18
		70:30	550	4H	P	22	25	27
3	System-3 (45%W/W) (Styrene)	90:10	600	H	P	25	27	31
		80:20	650	4H	P	28	29	33
		70:30	700	6H	P	31	33	35

* = 6H> 5H> 4H> 3H> 2H> 1H> H> HB> 1HB> 2HB> 3HB> 4HB> 5HB> 6HB⁶, P=pass and F=fail⁵⁻⁷.

Table-5: Flame-retardancy of the blended films.

Sr. No.	System	Blending Ratio (DGEBA: Vinyl ester resin)	UL-94	LOI (%)
1	System-1 (35%W/W) (Styrene)	90:10	V-1	20
2		80:20	V-0	22
3		70:30	V-0	23
1	System-2 (40%W/W) (Styrene)	90:10	V-1	22
2		80:20	V-0	26
3		70:30	V-0	28
1	System-3 (45%W/W) (Styrene)	90:10	V-0	30
2		80:20	V-0	32
3		70:30	V-0	33

Table-5 UL-94 and LOI it can be concluded that system-3 shows flame-retardant properties.

Conclusion

System-3 shows good scratch hardness, pencil hardness, chemical-resistance and flame-retardant properties.

References

1. Launikitis Matthew B. (1982). Vinyl Ester resins, Handbook of Composites. Springer US, 38-49, ISBN 978-1-4615-7141-4.
2. Patel R.H. and Patel H.B. (2007). Property modification of conventional castor oil based polyurethane using novel flame retardant polyurethane. *Prajna Journal of pure and applied science*, 15, 66-76.
3. Rosu L., Cascaval C.N. and Rosu D. (2009). Effect of UV radiation on some polymeric networks based on vinyl ester resin and modified lignin. *Polymer Testing*, 28(3), 296-300.
4. Shukla P. and Shrivastava D. (2014). Reaction kinetics of esterification of phenol-cardanol based epoxidized resins and methacrylic acid. *International Journal of Plastic Technology*, 18(1), 1-15.
5. Patel R.H., Shah M.D. and Patel H.B. (2011). Synthesis and Characterization of structurally modified Polyurethanes based on castor oil and Phosphorous-containing Polyol for Flame-retardant coating. *International Journal of Polymer Analysis and Characterization*, 16(2), 107-117.
6. Patel R.H., Patel H.B. and Shah M.D. (2009). Synthesis, Characterization and properties of flame-retardant Polyurethanes. *International Journal of Polymer Analysis and Characterization*, 14(6), 563-568.
7. Patel R.H. and Patel K.S. (2012). Synthesis and characterization of Polyesterurethanes and their applications to Flame-retardant coatings. *International Journal of Polymer Analysis and Characterization*, 17(1), 85-92