

Synthesis and Characterization of Novel Water-Soluble Polyesters for Electrical Insulation

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ABSTRACT: Polyesters based on poly(alkyl anhydride), aromatic anhydrides, and polyglycols were synthesized by thermal and catalytic condensation polymerization techniques. The polymerization conditions were optimized by the variation of the monomer concentration, reaction temperature, and so on to achieve the desired properties. The reaction was monitored by the measurement of the acid values at different stages of the polymerization reaction. The water solubility of these polyesters was achieved by the termina-

tion of the reaction with the addition of ammonia. These polyester resins were characterized with IR and viscosity measurements. The electrical properties of polyester resins coated and cured on glass cloth were measured with the idea of using them as impregnating varnishes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3309–3316, 2007

Key words: polycondensation; polyesters; water-soluble polymers

INTRODUCTION

Most insulating coatings used in the electrical industry are based on solvents, and organic solvents such as cresol, xylene, and naphtha are used.¹ These coatings have a disadvantage, in that the solvents are emitted in the form of hazardous vapors during the coating process. These vapors pollute the environment with their foul smell, toxicity, and highly flammable nature.^{2–4} Therefore, environmentally friendly insulation coatings are desired for electrical applications.⁵

Faced with this challenge, researchers have attempted to modify existing products or produce new ones that have lower solvent contents or are solvent-free or contain zero or low amounts of volatile organic compounds and hazardous air pollutants.⁶ There are basically three alternatives for formulating low-emission coating systems: powder coatings, high-solid coatings, and water-borne coatings.⁷ Recently, there has been momentum to develop cost-effective and nonhazardous water-based coatings. There are three general types of water-borne coatings:⁸ (1) water-soluble coatings, (2) water-reducible coatings, and (3) water-dispersible coatings. In a water-soluble coating, the polymer forms a homogeneous solution in water, and the coating is converted

into an insoluble form during curing. Water-reducible coatings contain copolymers formed by polymerization reactions that occur in water-miscible solvents such as alcohols or esters. Polar groups on the polymer allow water reducibility.⁷ In water-dispersible coatings, the vehicles consist of small particles of a binder distributed in a water medium (heterogeneous mixture).^{7,9} Water-borne polymers are of increasing importance (for coatings, adhesives, etc.) in an age in which organic solvents are perceived to be undesirable.¹⁰

Various attempts have been made to make polyester resins water-soluble.¹¹ One of the procedures involves the incorporation of polyvalent (at least trivalent) carboxylic acid groups into the main chain as a water-soluble portion. Another procedure is to sufficiently increase the OH/COOH ratio and limit the molecular weight to a certain extent so that the skeleton of the resin is rendered water-soluble before it becomes hydrophobic.¹² There is another novel technique in which a polyester resin is first prepared that is substantially equivalent to an organic solvent-type polyester, and the polyester resin is rendered water-soluble by the addition of a polybasic acid containing a single anhydride group to a side or terminal hydroxyl group of the resin to form a free carboxyl group.¹²

In this study, an effort was made to synthesize a water-soluble, insulating coating, which was prepared by the reaction of aromatic dicarboxylic acid and poly(hydric alcohol) components to produce polyester resins.^{2,6} These resins were made water-

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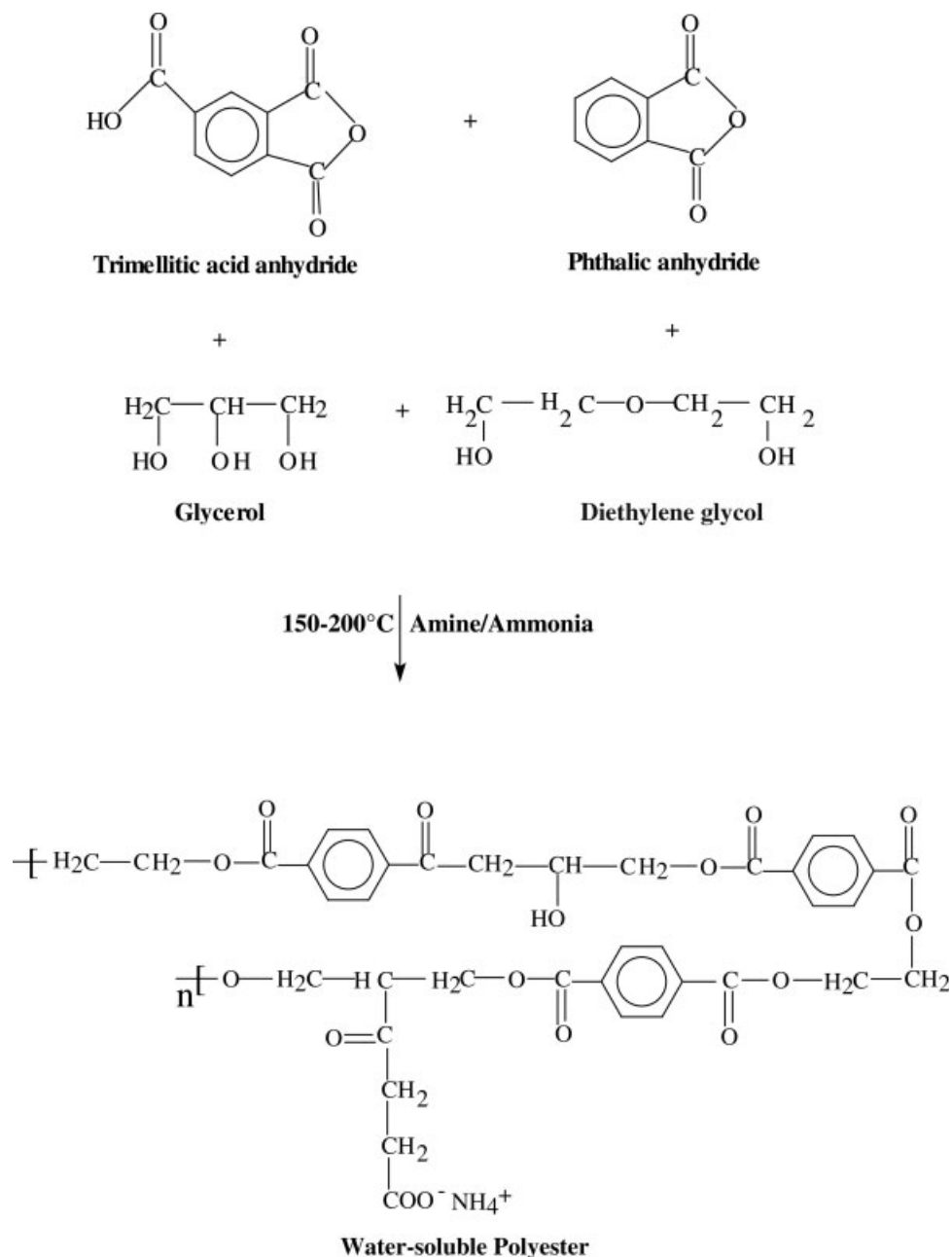


Figure 1 General schematic diagram for the synthesis of water-soluble polyester resins.

soluble by the enhancement of the carboxylic and amide groups in the polymer chains.

EXPERIMENTAL

Chemicals

Trimellitic acid anhydride (commercial-grade), phthalic anhydride (commercial-grade), adipic acid, terephthalic acid, diethylene glycol (analytical-reagent-grade), ethylene glycol (analytical-reagent-grade), glycerol (analytical-reagent-grade), neopentyl glycol, and *para*-toluene sulfonic acid were used.

Synthesis

The syntheses of the resins were carried out in a four-necked, round-bottom flask equipped with a thermometer socket, a glass stirrer with a Teflon paddle, and a Dean-Stark collector for water collection. Polyesters of acid anhydrides, aromatic anhydrides, and diols were prepared by condensation polymerization, with the range of polymerization kept between 150 and 200°C. The polymerization reaction was monitored by the continuous measurement of the acid value, and at a particular acid value, the ammonia solution was added; this resulted in the formation of a

TABLE I
Details of the Chemical Composition for Each Synthesis

Resin	Acids		Glycols			Catalyst PTSA (wt %)
	TMAA	PA	DEG	EG	G	
WPE-1	0.9	0.3	0.3	0.2	0.5	—
WPE-2	0.85	0.15	0.4	0.4	0.7	—
WPE-3	0.7	0.3	0.4	0.4	0.7	—
WPE-4	0.55	0.45	0.4	0.4	0.7	—
WPE-5	0.85	0.15	0.4	0.4	0.7	0.1
WPE-6	0.7	0.3	0.4	0.4	0.7	0.1
WPE-7	0.55	0.45	0.4	0.4	0.7	0.1

TMAA = trimellitic acid anhydride; PA = phthalic anhydride; DEG = diethylene glycol; EG = ethylene glycol; G = glycerol; PTSA = *para*-toluene sulfonic acid.

water-soluble resin. A schematic representation of this type of reaction is given in Figure 1.

Analysis

Nonvolatile matter

Weighing dishes of aluminum, approximately 51 mm in diameter and 16 mm high on the sides, were preheated for 15 min at 150°C to remove moisture. After these dishes were cooled to room temperature, they were weighed, and 1.5–1.6-g resin samples were poured into them. These dishes were reweighed and were placed in an oven at 135°C for 3 h. After complete drying, the dishes were cooled in a desiccator to room temperature and weighed again. The percentage of the nonvolatile matter was calculated:

$$\text{Nonvolatile matter} = \frac{\text{Weight of the residue}}{\text{Weight of the material}} \times 100$$

End-group analysis

End-group analysis of condensation polymers usually involves chemical methods of analysis for functional groups. Carboxyl groups in polyesters^{13,14} are titrated directly with a base in an alcoholic or phenolic solvent:

$$\text{Acid value} = 56.1 \times [(BR-B)/Wt] \times N$$

where N is the normality of the alcohol KOH, B is the blank reading, Wt is the weight of the resin sample, and BR is the Burette reading of the sample.

Viscosity measurements

Viscosity measurements were carried out with a no. 4 flow-cup viscometer (M/S. Associated Manufacturers Pvt. Ltd., New Delhi, India) according to the method mentioned in IS 3944-1982. A 150-mL resin sample and a flow cup were kept at $27 \pm 0.5^\circ\text{C}$.

With the orifice closed by a finger, the air-bubble-free sample was poured into the cup. If any bubbles formed, it was allowed to remain still until it became free of all air bubbles. A suitable receiver was placed under the flow cup so that the distance between the orifice of the flow cup and the surface of the received sample was not less than 100 mm. The finger was removed from the orifice, and the stop clock was simultaneously started. As soon as the first break was observed in the stream of the sample, the clock was stopped. The flow time was recorded to the nearest 0.2 s.

Dielectric strength

The samples for the analysis of the electrical properties were prepared with a glass cloth as a substrate per ASTM D 115-1985. Specimens 38 mm wide and 250 mm long were prepared from heat-cleaned woven fabric (style 116 listed in specification D 2518) with the length in the direction of the warp threads. Before the coating, the varnish was conditioned at the standard laboratory temperature for 4 h. The specimens were immersed in the varnish until the air-bubble formation stopped. Then, the specimens were withdrawn at 100 mm/min and drained in a dipping and draining chamber in the same position as they were dipped for 30 min. To facilitate dipping and curing and to obtain smoother specimens, the fiber glass strips were secured at both ends to a rectangular wire frame of about $240 \times 70 \text{ mm}^2$. These samples were then dried and cured in oven for about 4–6 h at 135–180°C for the first coat. The next coat was applied by reverse dipping; the samples were withdrawn as soon as they were immersed and allowed to drain as for the previous coat. Similarly to the first coat, the final one was allowed to bake to obtain a uniform coat.

Coated samples or test specimens were prepared and cured. Five to six measurements of the thickness for each specimen along the length of the sample were measured and recorded as average values. The brass electrodes, consisting of opposing cylindrical metal rods 6.1 mm in diameter with edges rounded to a radius of 0.8 mm, were placed in the wooden setup and polished before testing. The electrode

TABLE II
Acid Value Measurements

Resin	Acid value
WPE-2	197.56
WPE-3	233.35
WPE-4	242.83
WPE-5	182.00
WPE-6	159.62
WPE-7	134.15

TABLE III
Measurements of the Various Properties of the Polyester Resins

Resin	Properties				
	Viscosity (s)	Nonvolatile matter (%)	Dielectric strength (kV/mm)	Volume resistivity (Ω cm)	Tan δ
WPE-2	115	~57	34–39	$>4 \times 10^{16}$	0.0008
WPE-3	110	~57	49–50	$>5 \times 10^{16}$	0.0017
WPE-4	111	~59	32–36	$>1 \times 10^{16}$	0.0024
WPE-5	108	~61	30–32	$>2 \times 10^{15}$	0.0021
WPE-6	108	~60	50–58	$>2 \times 10^{15}$	0.0016
WPE-7	108	~54	46–53	$>2 \times 10^{15}$	0.0024

faces were kept parallel and held exactly opposite to one another. Each sample was kept between the two electrodes, and the applied voltage method was used to measure the voltage at $27 \pm 2^\circ\text{C}$. According to this method, the voltage was raised from zero at a uniform rate of 500 V/s (per test method D 149) so that breakdown would occur on average between 10 and 20 s. Five measurements of the breakdown voltage were taken, and the electric strength was calculated:

$$\text{Electric strength (kV/mm)} = \frac{\text{Breakdown voltage (kV)}}{\text{Average thickness (mm)}}$$

Volume resistivity

Coated samples were prepared; five measurements of the thickness of each specimen were measured,

and their average values were recorded. A high-resistance meter from Hewlett-Packard (model 4329A) (USA) was used for the measurements. One sample was inserted at a time into the sample holder (cell) with the coated surface in contact with the graded electrode and was charged for 1 min at 500 V (direct current). The volume resistivity measurements were carried out at $27 \pm 2^\circ\text{C}$:

$$\text{Volume resistivity } (\Omega \text{ cm}) = 19.6(R_v/t)$$

where R_v is the volume resistance (Ω) and t is the thickness (cm).

IR analysis

Samples for analysis were prepared with potassium bromide and resin pellets. The scans were obtained with a PerkinElmer Spectrum BX Fourier transform infrared (FTIR) system (Huenenberg, Switzerland).

RESULTS AND DISCUSSION

Synthesis of the polyester resins

The ratio of the reactants was varied to achieve the desired electrical properties. The acid or anhydride ratio was varied in the range of 1.0–1.2, whereas that of the glycol was varied in the range of 1.0–1.5, as mentioned in Table I. The characterization of the resin was carried out by FTIR and viscosity measurements. After samples of the resin were prepared on

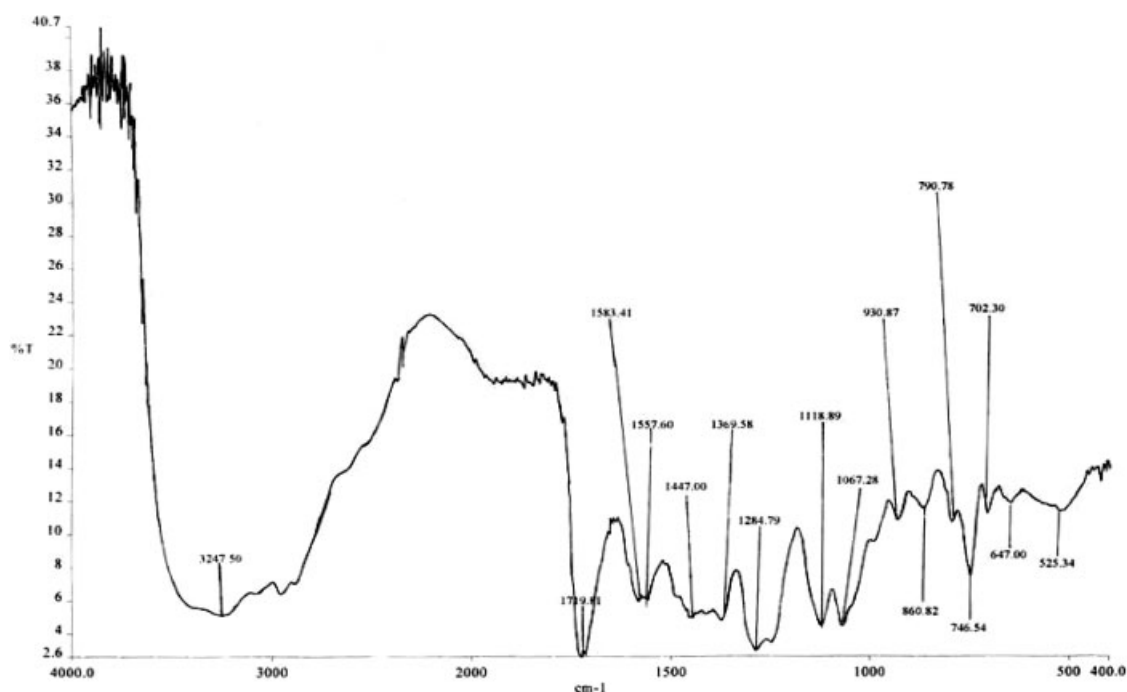


Figure 2 IR spectrum of WPE-2.

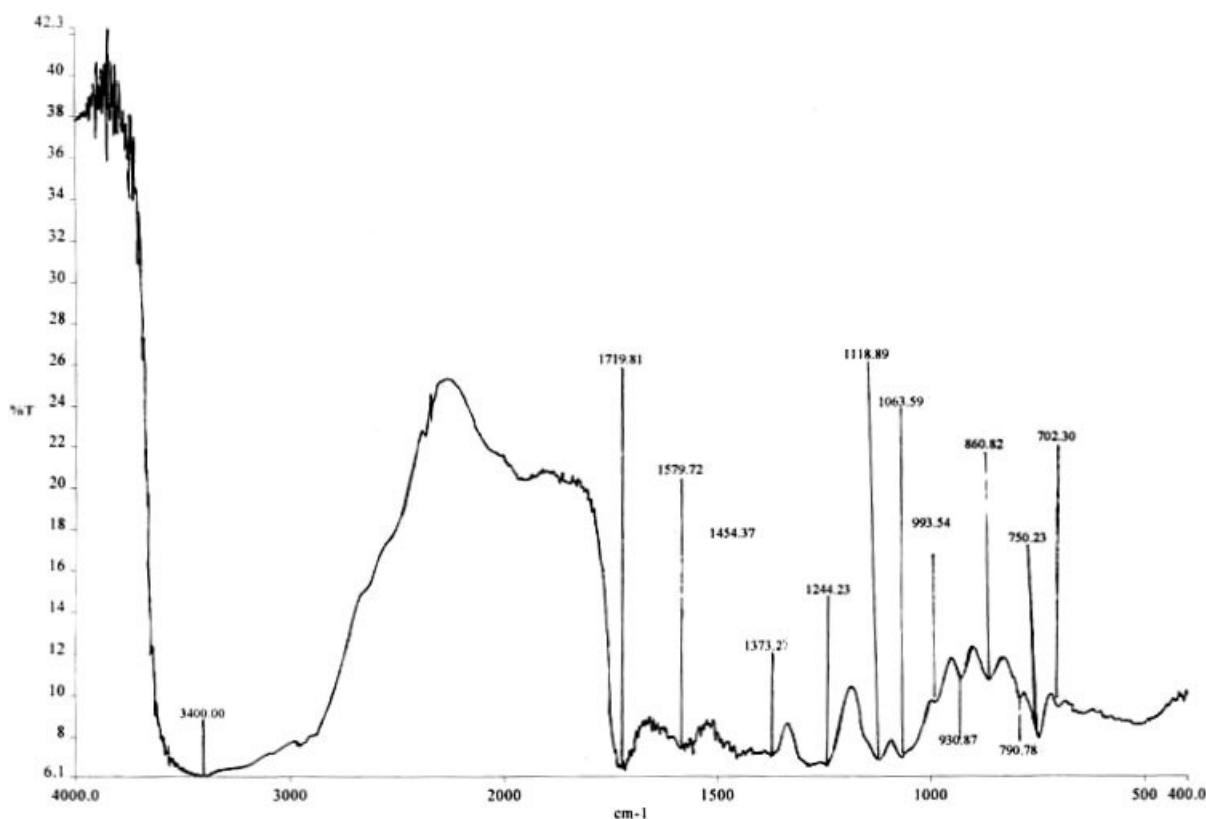


Figure 3 IR spectrum of WPE-3.

glass cloth, the properties of the resin, such as the breakdown voltage and volume resistivity, were studied.

The reactions carried out with an acid/glycol ratio of 1.2:1.0 (WPE-1, as mentioned in Table I) gelled within 30–40 min of the start of the reaction. This was because the rate of these reactions could not be controlled.

Acid value measurements

The acid values of the samples are tabulated in Table II.

Most of the reactions were terminated at higher acid values as the viscosity of the resins became too high and uncontrollable. In most of the information available from the literature, the polymerization reactions were terminated at lower acid values. However, we achieved water solubility at higher acid values of the polyester resins. This may have been due to the incomplete fusion of carboxylic and hydroxyl groups. From the results for WPE-2 to WPE-7, we observed that with the addition of the catalyst, the reactivity of the materials increased. Thus, the acid values of WPE-5 to WPE-7 fell even though the other reaction param-

eters remained the same. This was because more fusion of carboxyl and hydroxyl groups took place.

Characterization

The reactions were studied with and without the use of a catalyst with the intention of obtaining a polymer best suited for electrical-insulation applications.

Table III gives us the values of different electrical properties for six resin compositions measured while similar viscosities were maintained.

The best results were observed when the molar ratio of trimellitic acid anhydride was 0.7 mol, the molar ratio of phthalic anhydride was 0.3 mol, the molar ratio of diethylene glycol was 0.4 mol, the molar ratio of ethylene glycol was 0.4 mol, and the molar ratio of glycerol was 0.7 mol. The best dielectric strength (with or without a catalyst) was attained with this very composition, as mentioned in Table I, for WPE-3 (without a catalyst) and WPE-6 (with a catalyst).

The volume resistivity of the samples was higher when the reaction was carried out without a catalyst in comparison with the reactions in which a catalyst was used.

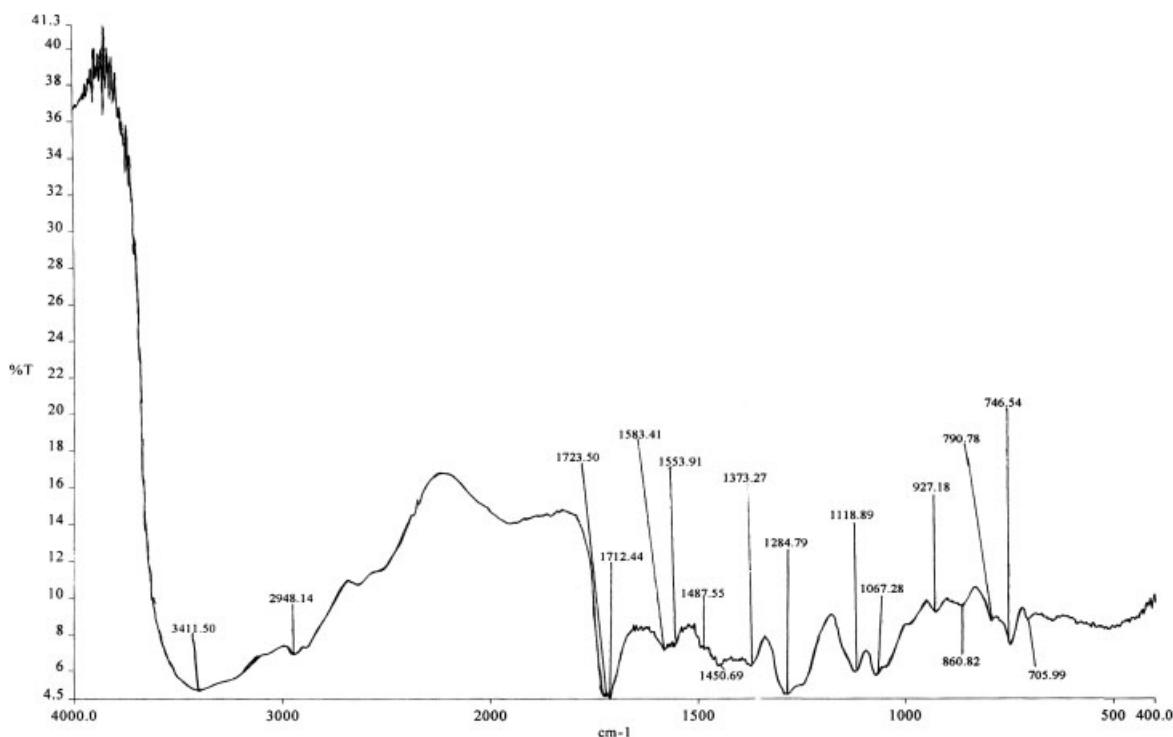


Figure 4 IR spectrum of WPE-4.

For WPE-2 to WPE-4, as the concentration of trimellitic acid anhydride increased, there was a decrease in the values of $\tan \delta$. The same trend was not observed in WPE-5 to WPE-7, for which a catalyst was used.

IR analysis

To confirm the presence of ester linkages and the formation of polyesters, IR spectra of samples WPE-2 to WPE-7 were taken and are shown in Figures 2–7. The stretching at 1719.81, 1719.81, 1723.50, 1719.81,

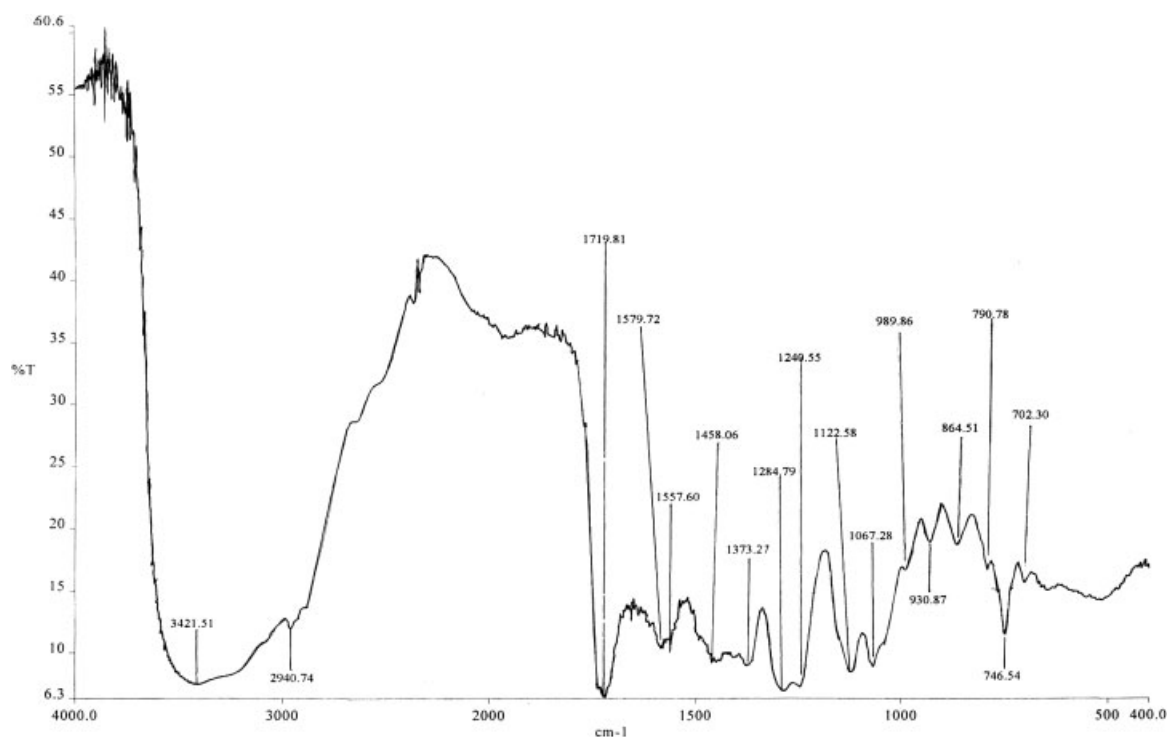


Figure 5 IR spectrum of WPE-5.

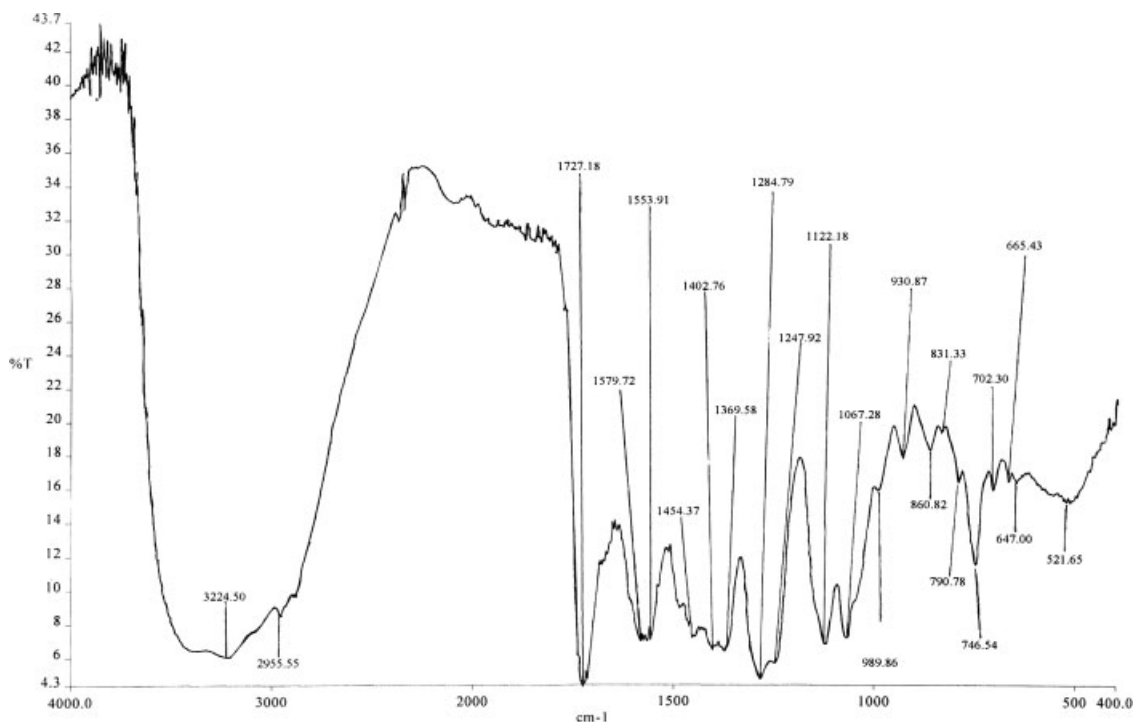


Figure 6 IR spectrum of WPE-6.

1727.18, and 1723.00 cm⁻¹ indicates the —C=O linkages.

CONCLUSIONS

The synthesized resins were completely soluble in all dilutions. The resins had properties that were

suitable for insulation and impregnation. Developments in waterborne products can be expected to continue to improve application and performance characteristics, providing product finishers with effective and important solutions to meet the challenge of compliance for volatile organic compounds.

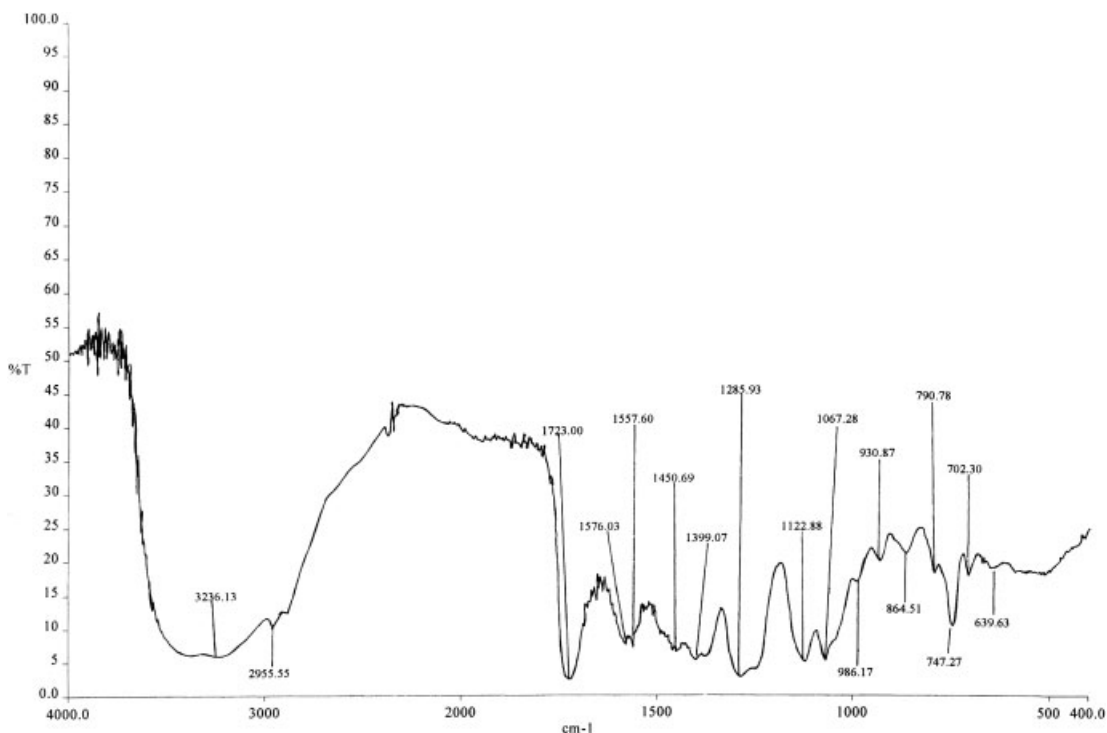


Figure 7 IR spectrum of WPE-7.

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