

Condensation Polymerization of Multifunctional Monomers and Properties of Related Polyester Resins.

II. Thermal Properties of Polyester-Imide Varnishes

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Synopsis

Polyester-imide prepolymers containing synthesized *N,N'*-bis(hydroxyethyl)pyromellitic diimide (PMDI) or *N,N'*-bis(hydroxyethyl)-3,3'-4,4'-benzophenone tetracarboxylic diimide (BTDI) were synthesized under conditions previously reported. One-component varnishes were obtained by mixing the synthesized prepolymers with commercial Desmodur CT-stable. Thermal behavior of these varnishes was investigated using thermogravimetric analysis. Activation energy of cured film, which was a polyester-imide varnish, was determined by using a multiple heating rate method. Polyester-imides coated copper wires were characterized, and were found to be acceptable, according to the specification of Japanese Industrial Standard (JIS-C-3214).

INTRODUCTION

In the early 1960s, polyester-imide varnishes were developed by the Dr. Beck Corp. in Germany and the Schenectady Chemical Co. in the United States. The polyester-imide was obtained by incorporating imide monomer units into a polyester main chain to modify the heat resistance of varnishes.

The polyester-imide resins, which were blended with crosslinker to form a one-component varnish, contain many properties which are better than those of the known alkyd resins. Polyester-imide resins also have better solubility and adhesive properties than the polyimide resins. When coated onto a copper wire, the enameled films of the ester-imide resins possess marked thermal stability, increased solvent resistance, hardness, and flexibility, and they are more economical than the corresponding polyamide or polyimide varnishes.¹

In this study, dicarboxylic diimides were prepared by benzophenone tetracarboxylic dianhydride or pyromellitic dianhydride and monoethanolamine. The imide product was mixed with respective monomers which were described previously.²

When Desmodur CT-stable (a phenol-blocked polyisocyanate) is used to make one-component varnish with polyester-imide, the cured film has a higher thermal degradation temperature than those of polyester varnishes. Thermal pyrolysis measurements of the cured synthesized polyester-imide

varnishes and the coating properties of resulting enameled wires are also discussed.

EXPERIMENTAL

Materials

Monomers used in synthesizing polyester-imide prepolymer were the same as those described in a previous study² except for trimethanolpropane (TMP) and 1,4-butanediol (BD). In addition, reagent grade pyromellitic dianhydride (PMDA) (Merck Co.) and a technical grade 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) (GAF Corp.) were used as dianhydrides. Reagent grade monoethanolamine was purchased from the Hayashi Chemical Industries, Japan. All chemicals were used without further purification.

Synthesis

The polyester-imide prepolymers (hydroxyl-ended polyurethane precursor) were prepared by solution polymerization technique using *m*-cresol as the solvent.

N,N'-bis(hydroxyethyl) pyromellitic diimide (PMDI) and *N,N'*-bis(hydroxyethyl)-3,3'-4,4'-benzophenone tetracarboxylic diimide (BTDI) were prepared by a method previously described.^{3,4}

The proper equivalence ratios of dimethyl terephthalate (DMT), ethylene glycol (EG), glycerin (G), diimide, and pentaerythritol (PE) were introduced into a 300-mL four-necked flask, equipped with a mechanical stirrer, nitrogen gas inlet, a condenser, and a thermocouple.

The catalyst was 1.4×10^{-3} mol % $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in DMT. The process of preparing the polyester-imide prepolymers was previously reported.²

Characteristic Tests

The melting point of synthesized diimides, purified after crystallization, was determined by using a DuPont 1090B thermal analyzer equipped with DSC 910, a heating rate of 10°C/min was used from 50–300°C under nitrogen.

The recrystallized diimides and the reprecipitated polyester-imide prepolymers (reprecipitated from the polymeric product by methanol) were dried in a 60°C vacuum oven and identified with an IR spectrometer in KBr pellet form. Coated onto aluminum foil to form a thin film, the 40% w/w varnishes were baked at 210°C for 15 min. The cooled, coated foils were dipped into a 1*N* HCl solution in order to etch the aluminum foil. The cured films were then analyzed with an IR spectrometer.

The IR spectrometer used was a Jasco A-202 model with a range from 4000 to 400 cm^{-1} .

Thermogravimetric analysis (TGA) measurements of polyester-imide varnishes cured film were made with a DuPont 1090B Thermal Analyzer equipped with a TGA 951 from room temperature to 800°C. A nitrogen atmosphere was used to determine the activation energy of pyrolysis.⁵ The IPDT (integral

procedural decomposition temperature)⁶ of samples (10 ± 1 mg) was evaluated from 30 to 900°C in nitrogen at a heating rate of 20°C/min.

Enamel Wire Coating

The procedure of coating the synthesized varnishes onto the copper wire is similar to that earlier reported.² The tests of magnetic wire for polyester-imide varnishes were based on a Japanese Industrial Standard (JIS-C-3214).⁷

RESULTS AND DISCUSSION

Synthesis of BTDI and PMDI

In the present work, diimides (either PMDI or BTDI) had been prepared by reacting dianhydride (either PMDA or BTDA) with monoethanolamine. Differential scanning calorimetry (DSC) of purified BTDI shows a melting point near 210.5 and 277.6°C for synthesized PMDI. Synthesis of polyester-imide varnishes by the reaction of diimides (either BTDI or PMDI) with DMT, EG, G, and PE was previously described.² Also, the coating procedure and thermal properties of these polymers were also previously described.²

KBr pellets were used for IR measurements of BTDI. The IR characteristic band of the imide group (the imide IR absorption peak had been reported to occur between 1810 and 1775 cm^{-1}) was observed at 1720 and 1780 cm^{-1} ($-\text{CO}-$ of imide stretching vibration).⁸ The other prominent absorptions of the imide ring (1380 and 720 cm^{-1}), and $-\text{OH}$ (3600 cm^{-1}) were also observed, as shown in Figure 1.

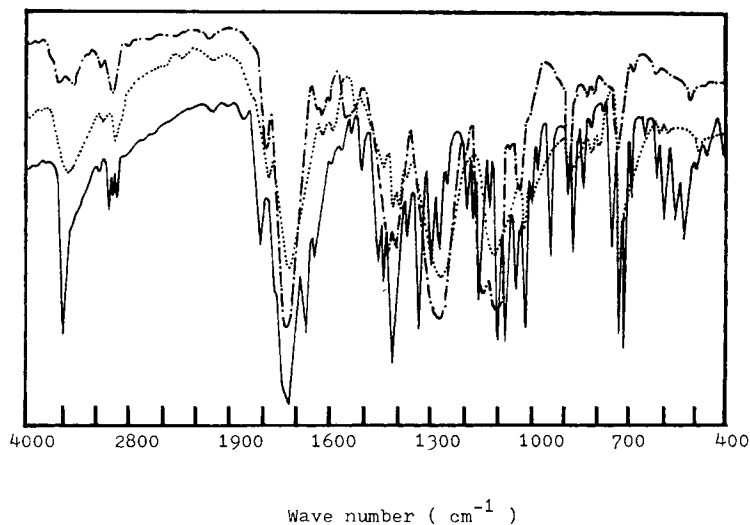


Fig. 1. The IR spectra of *N,N'*-bis(hydroxylethyl)-3,3'-4,4'-benzophenone tetracarboxyl diimide (—), synthetic PE-BTDI prepolymer (···), and the crosslinked film (— · — · —) prepared from PE-BTDI prepolymer with CT-stable at 210°C for 15 min.

Synthesis and IR Spectra of Polyester-Imide Prepolymers and Their Cured Films

The preparation of polyester-imide prepolymers was accomplished by mixing DMT, EG, G, PE diimides at the proper equivalence ratios and polymerizing using the same condition as that discussed in Part I.² The resulting prepolymers, having a partly imide structure, were expected to modify the heat resistance of cured film (obtained from mixing prepolymer with CT-stable and then cured at 210°C) when applied as a one-component varnish. Figure 1 also shows the IR spectrum of polyester-imide (PE-BTDI) prepolymer, reprecipitated from methanol. The IR spectrum clearly shows the typical absorption peaks of polyester-imide backbone. The most characteristic absorption peaks of imide were found at 1780–1770 cm^{-1} and 1730–1700 cm^{-1} ; those of the aliphatic CH and N—CH stretching of diimide at 2920–2800 cm^{-1} ; those of diimide aromatic ring at 1600–1450 cm^{-1} and 690–750 cm^{-1} ; and those of the aliphatic C—N stretching at 1350–1000 cm^{-1} . The additional broad peak between 3500 and 3300 cm^{-1} indicates the presence of the hydroxyl functional group in the resultant polyester-imide, supplying the crosslinked linkage.

The detectable characteristic absorption peaks of cured synthesized varnish, shown in Figure 1, are at 3350 cm^{-1} for N—H stretching; 2950 and 2850 cm^{-1} for aliphatic C—H stretching; 1730 cm^{-1} for C=O stretching of urethane and carbonyl structure; and 1640 cm^{-1} for C—N. The N—H in-plane bending vibration mode indicates that the cured film has the structure backbone in conformity with those which have been mentioned.

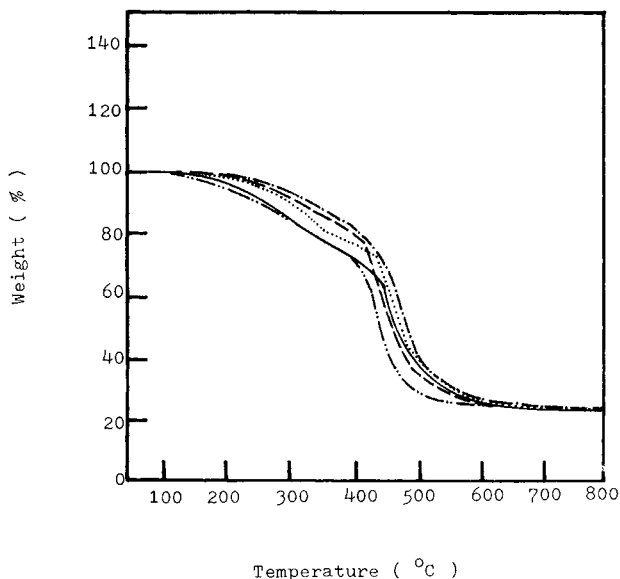


Fig. 2. Thermogravimetric traces in nitrogen atmosphere of PE-BTDI varnish cured at 210°C for 15 min with the following heatup rates ($^{\circ}\text{C}/\text{min}$): (.....)10; (---)20; (—)30; (···)40; (-----) 50.

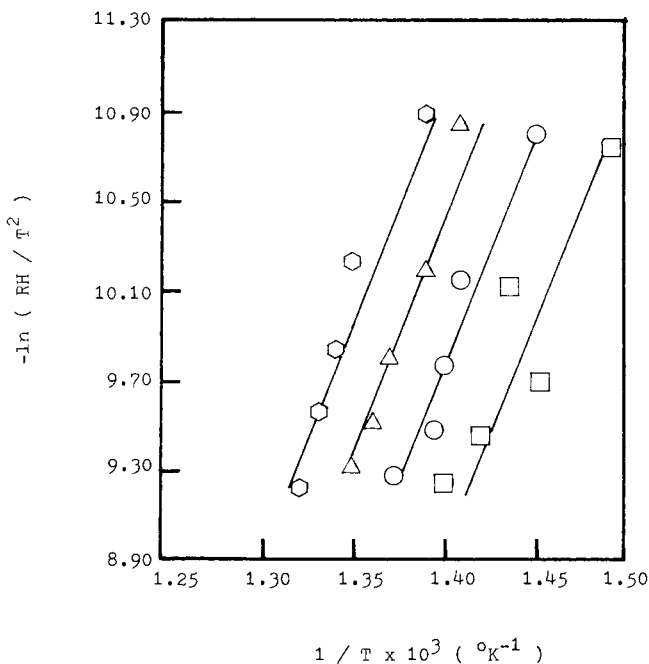


Fig. 3. Determination of activation energy for different weight loss of cured PE-BTDI varnish at different heating rates (RH). Weight loss: (○) 60%; (△) 50%; (◇) 40%; (□) 30%.

Thermal Behavior of Polyester-Imide Varnishes Cured Film

The temperature characteristics of cured films (obtained from polyester-imide varnishes), such as T_0 (initial decomposition temperature), T_{10} (temperature for 10% weight loss), T_{50} , and T_{max} (temperature for maximum rate of decomposition) were determined with TGA thermograms (Figs. 2 and 4). The T_0 and T_{10} are among the main criteria for determining the heat stability of polymers (with dynamic heating)⁸; the higher the value of T_0 and T_{10} , the higher the heat stability of a given polymer. The film obtained from PE-BTDI varnish exhibited 10% weight loss at 328°C, and the residual weight at 800°C was about 24% of the original weight. Also, 10% weight loss occurred at 281°C and residual weight of cured PE-PMDI varnish was 21.7%. As for the imide components, BTDI produced more stable crosslinked polymer than for the PMDI.

T_0 , T_{10} , and T_{max} are feature criteria, and, therefore, it is possible to correlate the thermal stability with the integral procedural decomposition temperature (IDPT) measurement to obtain a quantitative indication of the relative stability of crosslinked films. The IPDT is an index of thermal stability in terms of decomposition temperature, proposed by Doyle.⁶ The IPDTs of cured varnishes were calculated and found to be 435.6°C for PE-BTDI varnish and 405.7°C for PE-PMDI varnish.

The higher IPDT of PE-BTDI film than PE-PMDI film is in agreement with their thermal behavior at 50% weight loss. The quantitative criteria of

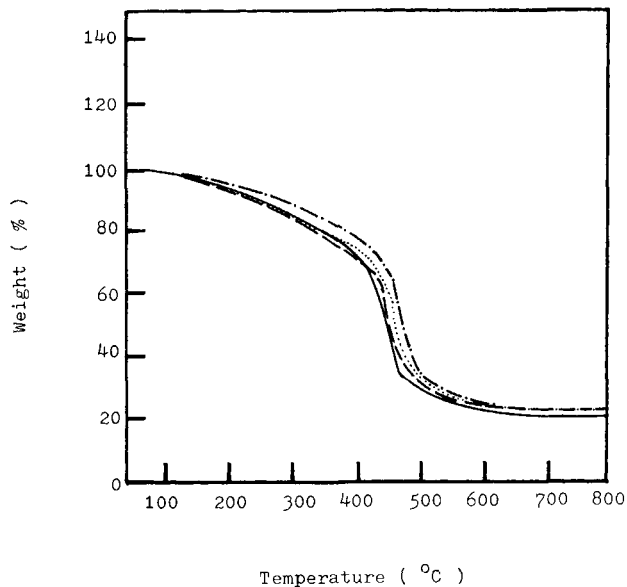


Fig. 4. Thermogravimetric traces in nitrogen atmosphere of PE-PMDI varnish cured at 210°C for 15 min with the following heatup rates (°C/min) (—) 20; (---) 30; (···) 40; (-·-·-) 50.

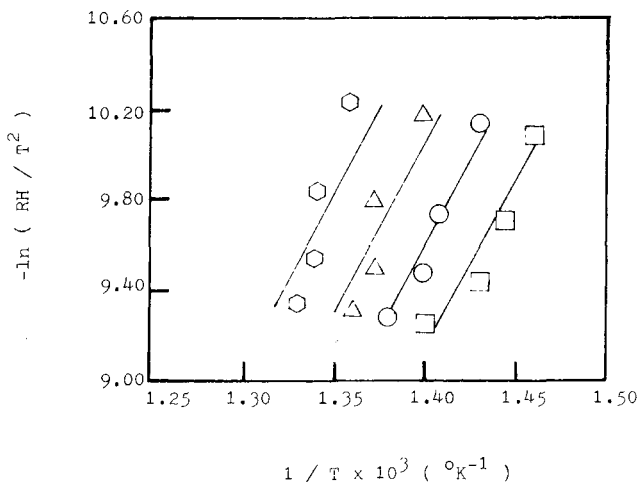


Fig. 5. Determination of activation energy for different weight loss of cured PE-PMDI varnish at different heating rates (RH). Weight loss: (○) 60%; (△) 50%; (◻) 40%; (◊) 30%.

thermal stability (IPDT) show the superior heat resistance of the PE-BTDI varnish cured film as compared with that of PE-PMDI cured film.

Investigation of the Activation Energy of Polyester-Imide Varnishes Crosslinked Film

The activation energy for decomposition (E^*) was calculated according to the method devised by Reich.⁹ Figures 2 and 4 show the TGA traces of the

polyester-imide varnishes cured film shift from left to right systematically with the increase of the heating rate, and the experimental results appear to be in accordance with the expected behavior, especially over the range of the weight loss from 40 to 70%, as can be seen in Figures 3 and 5. According to Reich,⁹ the activation energies of crosslinked films were calculated and these values were 169.6 and 116.4 kJ/mol for PE-BTDI and PE-PMDI varnishes, respectively. From these data it is revealed that BTDI gives more thermal stable polyester-imide than PMDI. These results are similar to those obtained by Choi and Choi³ but are in disagreement with those reported by Dine-Hart and Wright.¹⁰

Test Results of the Enamel Wires

From the test results of magnet wires, it is found that both varnishes have excellent properties in pinhole test, flexibility, aging test, and heat shock test; however, the magnet wire, coated by PE-PMDI varnish, can only be coated three times to avoid poor flexibility.

CONCLUSION

This study presents the synthesis of polyester-imide prepolymers by polycondensation of EG, G, PE, and synthesis of diimides with DMT. The one-component varnishes were prepared by mixing CT-stable with synthesized prepolymers. The integral procedural decomposition temperature (IDPT) and pyrolysis activation energy (E^*) of the cured varnishes were measured. From those results, it is found that PE-BTDI has a higher thermal stability than that of PE-PMDI. When coated onto pretreated copper wires to form magnetic enamels, the properties of these resins are acceptable by the JIS-C-3214 Standard Procedure.

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