

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

WEN-YEN CHIANG and WEN-CHANG CHIANG, *Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Road, 3rd. Sec., Taipei 10451, Taiwan, Republic of China*

Synopsis

This article discusses optimum conditions for polycondensation of multifunctional monomers. Reaction variables such as monomer concentration, temperature, and time were studied to optimize reaction conditions. The influence of the nature and concentration of catalysts was also investigated. The optimum reaction conditions consisted of polymerization in an 82% w/w *m*-cresol solution at 160°C for 2 h, continuous reaction at 200°C for 1.5 h at 230°C for 3.5 h, followed by 40 min under reduced pressure and at 200°C. The catalyst was 1.4×10^{-3} mol % $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in dimethyl terephthalate. Polycondensation of ethylene glycol, 1,4-butanediol, pentaerythritol, and trifunctional monomers (glycerin or trimethanolpropane) with dimethyl terephthalate was carried out in *m*-cresol to produce polyester prepolymers. The synthesized prepolymers were mixed with commercial Desmodur CT-stable (a phenol-blocked polyisocyanate) to form one-component varnishes which were characterized by thermogravimetric analysis. Polyester modified with trimethanolpropane has higher thermal stability than the one modified with glycerin. After being coated onto treated copper wires, the magnetic wires were characterized according to the specification of Japanese Industrial Standards (JIS-C-2358) and were found to be acceptable.

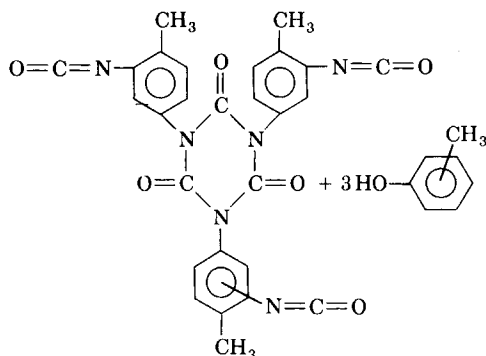
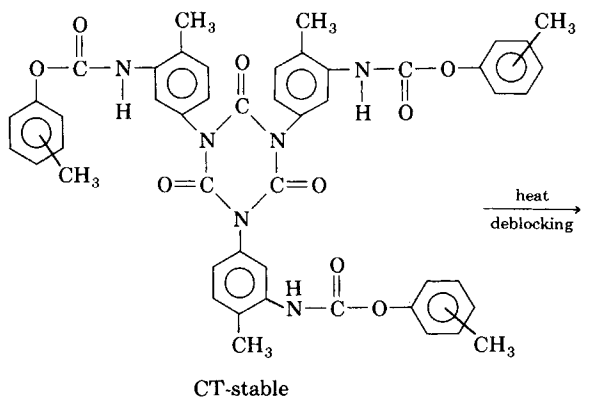
INTRODUCTION

Polyurethane varnish for enamel wire based on polyester prepolymers is widely used in the electrical industry. The excellent dielectric properties of the polyester film combined with its high strength, flexibility, and hydrolytic stability provide a superior insulating system.¹

Conventional urethane coatings can be either one-component or two-component coating.² In this study, synthesized polyester varnish (i.e., blocked polyisocyanate coating), which is a one-component coating, is considered and discussed. A polyester prepolymer based on dimethyl terephthalate (DMT) and ethylene glycol (EG) was further modified by the addition of multifunctional monomers, such as glycerin (G), 1,4-butanediol (BD), and pentaerythritol (PE). The main objective of this study is to investigate optimum polycondensation conditions. Refractive index and Brookfield viscosity were used to monitor the polymerization reaction³ in the hope that the results may be applied to mass production of the varnish for wire insulation coating.

Based on the optimum condition of this study, polyester prepolymers were modified with multifunctional monomers such as G, trimethanolpropane (TMP), and PE. The mixing was effected with CT-stable (a phenol-blocked

polyisocyanate) to form one-component varnishes. In order to investigate the curing condition of the synthesized varnishes, deblocking reaction of the commercial CT-stable (its reaction scheme is shown below), which leads to freeing -NCO groups with the liberation of the blocking agent, will also be discussed:



The thermal behavior of the cured varnishes was characterized. In addition, coating properties of magnetic wires which were coated with the synthesized varnishes and cured at 210°C for 15 min were tested following the JIS-C-2358 Standard Procedure.

EXPERIMENTAL

Materials

Monomers used in synthesizing polyester prepolymer were dimethyl terephthalate (DMT), technical grade, a commercial product of China Petrochemical Development Corp. (Republic of China). The glycols were a reagent grade ethylene glycol (EG), purchased from Union Tech. Chemical Co., Taiwan, and a reagent grade 1,4-butanediol (BD), purchased from Merck Co. The modifier glycols were a reagent grade glycerin (G), purchased from Kanto Chemical CO. (Japan); a reagent grade trimethanolpropane (TMP) purchased

from Hayashi Pure Chemical Industries Ltd. (Japan) and a technical grade pentaerythritol (PE), obtained from the Tatung Co. (Taiwan).

Reagent grade zinc acetate dianhydride $Zn(OAc)_2 \cdot 2H_2O$ purchased from Waco Ltd. (Japan) was used as catalyst. *m*-Cresol (MC-800) from Tatung Co. was used as solvent for polycondensation reaction.

Desmodur CT-stable, supplied by the Tatung Co., was used as crosslinking agent. It was prepared as a 40% w/w solution in *m*-cresol before being combined with the polyester resin. All chemicals were used without further purification.

Synthesis

The detailed process of preparing the polyester prepolymers (hydroxy-ended polyurethane precursor) by solution polymerization using *m*-cresol as the solvent has been reported.⁴

The proper equivalence ratios of DMT, EG, BD, PE, and trifunctional monomer were introduced into a 300-mL four-necked flask which was equipped with a mechanical stirrer, a nitrogen gas inlet, a condenser to receive the condensed distillate, and a thermocouple.

After the catalyst was added, the polycondensation reaction was carried out at a relatively high temperature for a given period of time. After reaction was completed, the system was maintained at 200°C again for a given period of time under reduced pressure (about 20 mm Hg).

Characterization

Absolute refractive indices were measured with a thermostated Abbe Refractometer (ATAGO Co. Ltd., Japan), maintained at a constant temperature of 28°C.

IR absorption spectra of polyester prepolymer and cured varnish films were obtained with an infrared spectrophotometer (Jasco A-202 model) in the range 4000–400 cm^{-1} .

The DSC measurements were carried out under air using a DuPont 1090B thermal analyzer coupled with a 910 differential scanning calorimeter (DSC). The size of the samples varied from 5 to 10 mg.

Brookfield viscosity of the synthesized prepolymers was measured with a Brookfield viscometer (LVF model), in a constant-temperature bath.

Thermal degradation of the crosslinked film of polyester varnishes from room temperature to 800°C was investigated with a DuPont TGA 951 equipped with a 1090B thermal analyzer. Experiments were carried out under nitrogen at a heating rate of 20°C/min. Sample size of 15 ± 1 mg was also used.

Enamel Wire Coating

The procedure for coating the synthesized varnishes onto the copper wire is as follows: A 40% w/w solution (*m*-cresol/xylene, 3/2 w/w) of polyester varnish was prepared by mixing polyester prepolymer with commercial Desmodur CT-stable at a ratio of 8/2 (w/w) in a test tube. Then an annealed, degreased copper wire (0.55 mm in diameter and 20 cm long) was dipped into the varnish and pulled through a small die (0.58 mm in diameter) at room

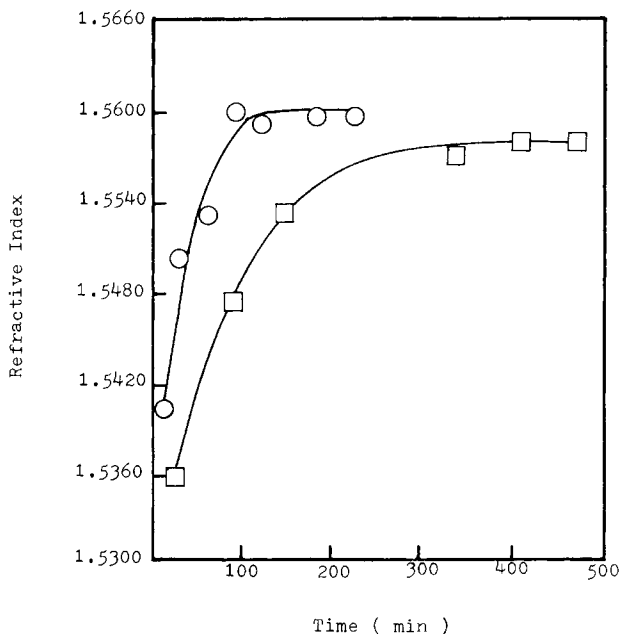


Fig. 1. Refractive index as a function of polymerization time for synthesized polyester prepolymer in different *m*-cresol systems at 210°C (w/w): (○) 82%; (□) 55%.

temperature. After putting the coated wire into an air-circulated oven and baked at 210°C for 15 min, the procedure was repeated four times, with the die slightly enlarged each time (0.60, 0.63, and 0.67 mm). The resulting polyurethane enamel wire had a diameter of 0.65 mm.

The coated wire was evaluated using the Japan Industrial Standard (JIS-C-2358, a specification of varnish for polyester copper wires).⁵ In addition, synthesized polyester resins were used in an industrial-scale enameled wire processing in the Enamel Wire Center of Tatung Co. (Taiwan); then the product wires were characterized following the same standard procedure.

RESULTS AND DISCUSSION

Polycondensation Condition

It has been shown that the high temperature solution polymerization is very useful for the synthesis of polyester prepolymers. Singh and Ohri³ had mentioned that the degree of polymerization can be monitored by the refractive index of the polymeric system; therefore, this method was used to determine the end point of polymerization. Solution polycondensation was first carried out at an elevated temperature to optimize reaction condition. Changes in refractive index as a function of polymerization time at two monomer concentrations (w/w) are shown in Figure 1. The refractive index of the system with 55% w/w solution reached on equilibrium after 180 min, whereas the system with a higher monomer concentration (82% w/w) had a higher refractive index and reached the equilibrium in less than 100 min.

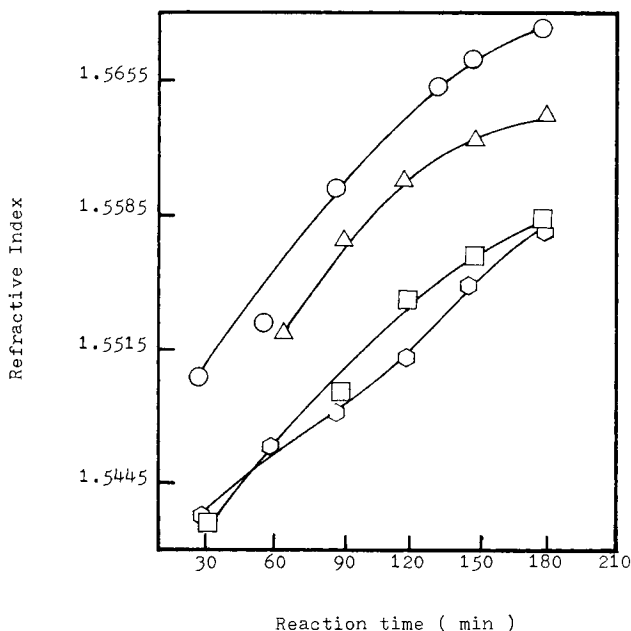


Fig. 2. Refractive index as a function of reaction time for synthesizing polyester prepolymer at various temperatures ($^{\circ}\text{C}$): (○) 230; (△) 220; (□) 210; (○) 200.

The effect of reaction temperature on the refractive index of the system was examined in *m*-cresol over the temperature range from 200 to 230 $^{\circ}\text{C}$. As shown in Figure 2, higher reaction temperature was highly beneficial for producing the high molecular weight polymer. This is probably due to increased molecular motion at high temperature, and, as a result, the rapid exchange of ester, bringing about a higher degree of polymerization.

The Brookfield viscosity as a function of polycondensation temperature is shown in Figure 3, for the system with 40% w/w solution. The viscosity of the system increased with the polymerization temperature. This result is in agreement with that shown in Figure 2. After reacting at high temperature and continuous reaction under reduced pressure at 200 $^{\circ}\text{C}$, the effect of distilling time on prepolymers viscosity was investigated. Brookfield viscosities of the resulting prepolymer solution at various temperatures (Fig.4) indicate that degree of polymerization was improved when reaction time is increased under reduced pressure system. This can be explained as a shift of polyesterification equilibrium by the small molecules released from the system forcing the reaction to produce more product. Thus, under a fixed set of conditions, the distillation time required for obtaining a higher viscosity was 40 min under the reduced pressure system (affected by a water aspirator).

Monomers were polymerized into polyester prepolymer using various catalytic systems, as the reaction proceeds very slowly in the absence of any catalyst. The rate of this reaction is greatly influenced by the nature of the polycondensation catalyst. This effect was studied by polymerizing the monomer under a fixed condition using a catalyst concentration of 1.4×10^{-3} mol metal ion/mole DMT. At the end of the experiment, the conversion (defined

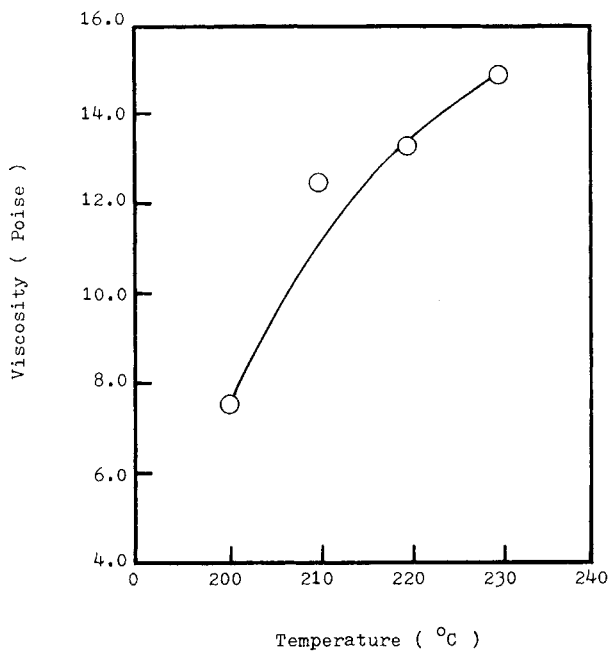


Fig. 3. Brookfield viscosity as a function of polycondensation temperature after 3.0 h at a 40% concentration of *m*-cresol.

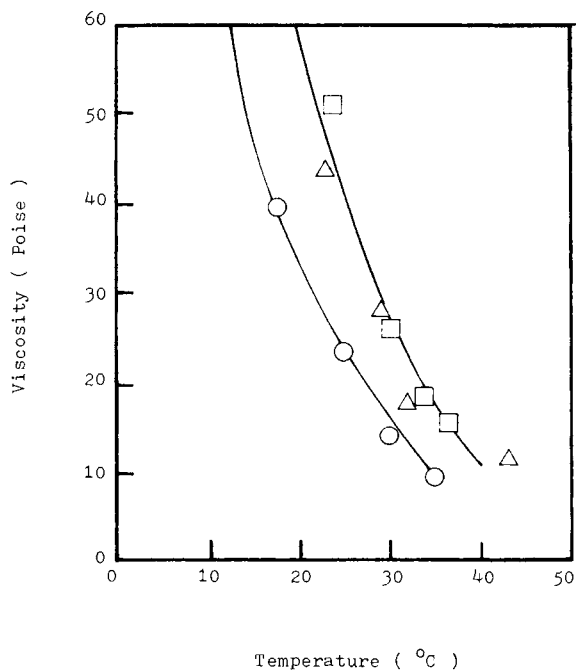


Fig. 4. Brookfield viscosity of 40% *m*-cresol solution as a function of temperature: (○) reduced pressure distillate for 15 min; (Δ) for 25 min; (□) for 40 min.

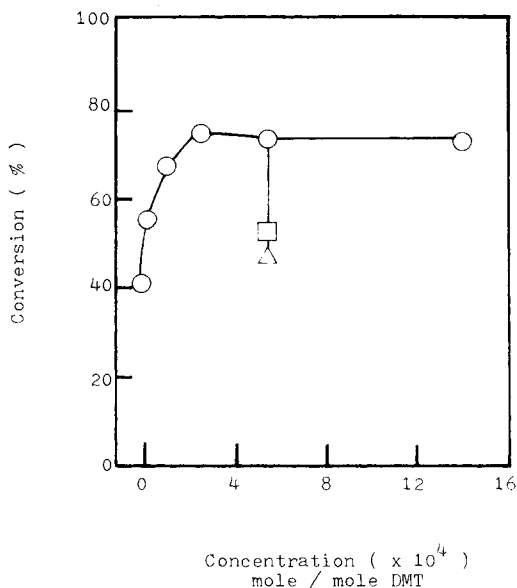


Fig. 5. Polymerization conversion vs. catalyst concentration and type: (○) Zn $(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$; (□) Mg $(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$; (△) Co $(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$.

as the amount of product, cured polymeric solution at 200°C for 2 h, as a percent of theoretical product) of the polymer formed was determined, and the findings were used as a guide to catalyst activity. The activity of the polycondensation catalysts increase in the order: Zn > Mg > Co.

Griehl and Schnock⁶ had discussed the order of catalyst effect on poly(ethylene terephthalate) precondensation in some detail. The results shown in Figures 5 and 6 indicate that zinc acetate is the most effective transesterification catalyst in the polycondensation of polyester prepolymer. The above order of catalytic activity is similar to that reported previously.⁶

The dependence of the polycondensation rate on the catalyst concentration in the range up to 5.6×10^{-3} mol % metal ion in DMT has been investigated. The results presented in Figures 5 and 7 show the effect of catalyst concentration on the conversion of the prepolymer formed at 230°C. It was found that the approximate optimum catalyst concentration is 1.4×10^{-3} mol % by DMT.

Polyester Varnishes

In coating systems, the curing temperature depends upon the type of blocking agent, as well as the nature of the attacking group. In general, curing of hydroxyl resins with phenol blocked isocyanates requires a temperature of about 150°C for about 30 min. Longer curing times at slightly lower temperature or shorter curing times at temperature as high as about 200°C may also be satisfactory.

The commonly used commercial crosslinkers of one-component polyurethane coating are Desmodur AP-stable and CT-stable. The deblocking reaction of AP-stable and the thermal behavior of the one-component varnish

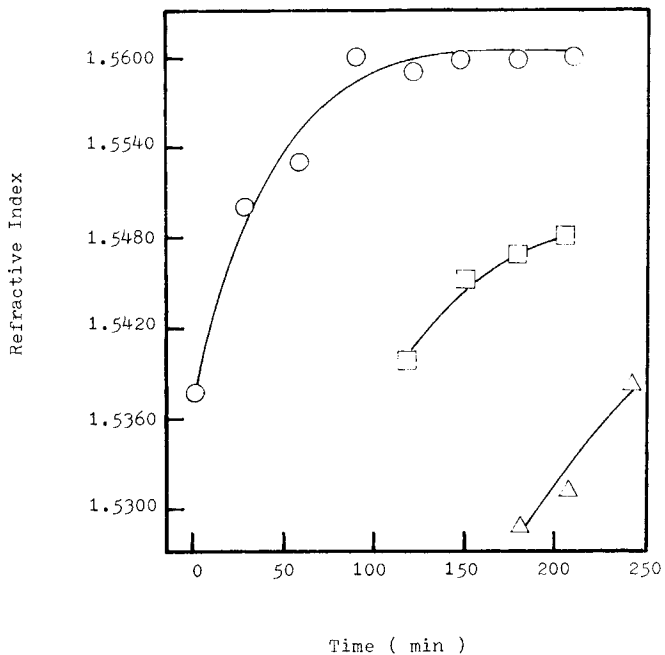


Fig. 6. The dependence of refractive indexes at 28°C on catalyst type (concentration = 5.6×10^{-4} mol/DMT): (○) Zn $(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$; (□) Mg $(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$; (△) Co $(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$.

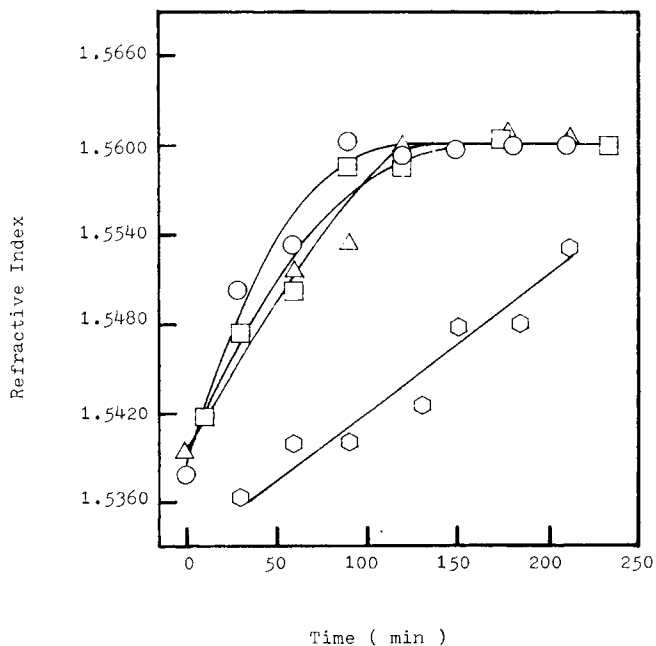


Fig. 7. Refractive index dependence on catalyst concentration [mol Zn $(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ /mol DMT]: (○) 14×10^{-4} ; (□) 5.6×10^{-4} ; (△) 2.5×10^{-4} ; (◇) 1.3×10^{-4} .

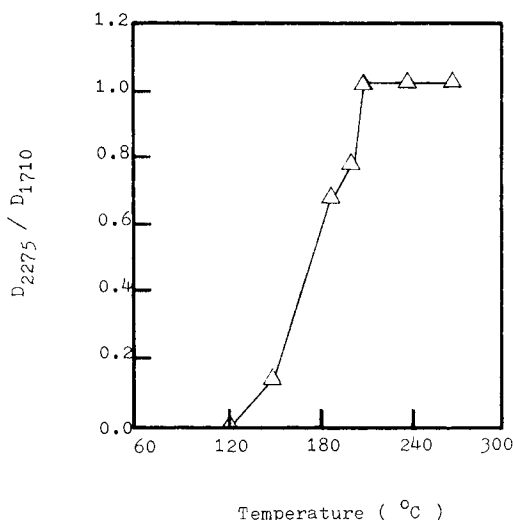


Fig. 8. Extent of deblocking reaction vs. bake temperature for 40% CT-stable. The curing time was 15 min.

of polyurethane incorporated with AP-stable have been discussed by Yang and Lee.⁷ In this study, the deblocking of commercial CT-stable is discussed. Its reaction scheme was described earlier.

The 40% w/w CT-stable in *m*-cresol reacted at different temperatures for 15 min was coated on a KBr window, and the IR spectrum obtained. Kinjo et al.⁸ reported that the IR characteristic absorption of carbonyl group of isocyanurate ring was 1710 cm^{-1} (stretching vibration), and that of isocyanate was 2275 cm^{-1} . As the isocyanurate ring is a thermal stable structure, the CT-stable proceeds deblocking reaction under thermal treatment and releases the blocked reagent to obtain the free isocyanate group. Therefore, the characteristic band of the isocyanurate ring at 1710 cm^{-1} was used as a standard, and the intensity of IR spectrum of the produced isocyanate group at 2275 cm^{-1} was found by the relative intensity change of isocyanurate/isocyanate. The results are plotted in Figures 8 and 9, in which the relative intensity change is plotted against the reaction temperature and/or heating time. From the experiments no isocyanate was observed in the KBr window before 120°C ; however, when the sample was heated over that temperature, the amount of isocyanate increased slightly, and the ratio of relative intensity reached a significant value after being heated at 210°C .

After heating at 210°C and after the blocking agent (para or meta cresol) was evaporated, a deblocking isocyanurate was obtained. Figure 9 shows the presence of isocyanate groups and the retention of the isocyanurate ring. From the result, it can be concluded that the proper deblocking time of CT-stable is 15 min.

IR Investigation of Synthesized Polyester Prepolymer and Their Cured Films

IR spectra of synthesized polyester prepolymers and those of crosslinked films are shown in Figure 10. The absorption peak at 3500 cm^{-1} is believed to

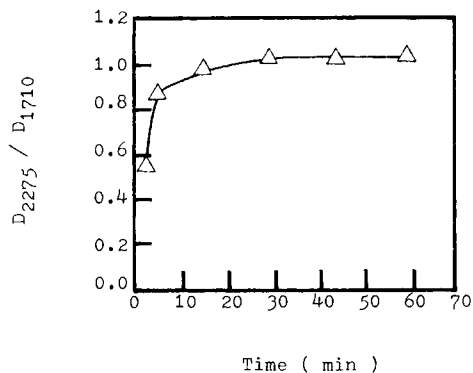


Fig. 9. Extent of deblocking reaction vs. bake time at bake temperature equal to 210°C for a 40% CT-stable.

be the skeletal stretching mode of the hydroxyl group and that at 1720 cm^{-1} , the C=O stretching of the carbonyl group. The detectable characteristic absorption peaks 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. Furthermore, N—H in plane bending vibration mode indicates that the cured film has a polyurethane structure.

Thermal Degradation of Polyester Crosslinked Film

Thermal behavior of polyester varnish crosslinked films, as modified by glycerin and TMP separately, were examined with thermogravimetric traces at a heating rate of 20°C/min. The results are shown in Figure 11. It indicates that the temperature of 50% weight loss for glycerin modified varnish is

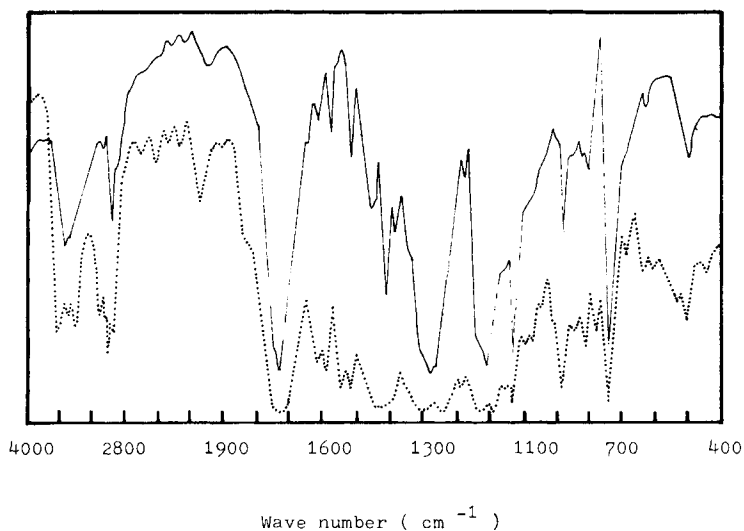


Fig. 10. Infrared spectrum of synthetic glycerin modified polyester prepolymer (—) and its cured films at 210°C for 15 min (···).

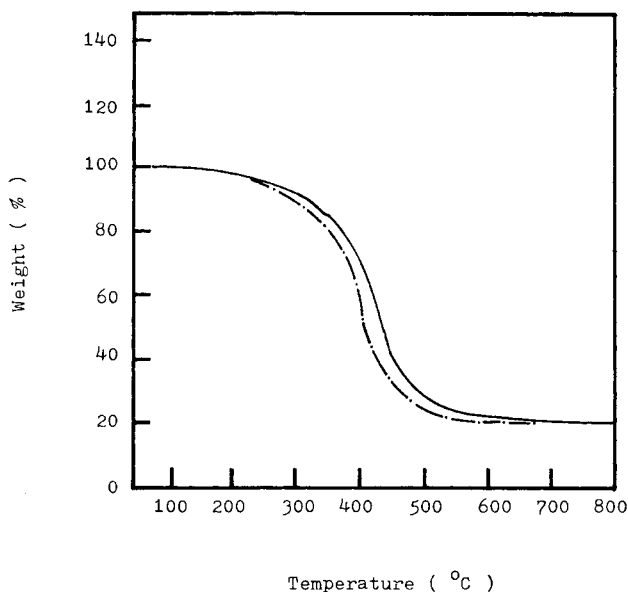


Fig. 11. Thermogravimetric traces in nitrogen atmosphere of polyester varnishes modified with glycerin (---) and TMP (—) cured at 210°C for 150 min.

410°C, and that of TMP modified varnish is 454°C. These results show that the latter has a higher thermal stability than the former.

Test Results of the Synthesized Varnishes and Enamel Wires

The Brookfield viscosities of the synthesized resins with 40% w/w concentration are 29 and 35 P for G and TMP modified prepolymers at 30°C, respectively. After coated onto copper wire, no cracks occurred on the enameled wires using the pin hole tests (the insulating property was checked with 12 V DC in a 0.2% NaCl aqueous solution; phenolphthalein was used as the indicator). The same results were obtained by the aging and heat shock tests (in the former, the specimens were placed in an air-circulated oven at 170°C for 6 h and then wound; in the latter, the samples were placed in the oven at 130°C for 2 h after winding on a mandrel whose diameter was three times that of the samples). The coated films showed excellent chemical resistance and adhesiveness for more than 14 days in 1.2 s.g. H₂SO₄, 1% w/w NaOH aqueous solution, mineral oil, and benzene, respectively. The insulating breakdown voltages of the enameled wires were about 7 KV. It was found that all varnishes modified with glycerin or TMP showed excellent properties in the pinhole test, flexibility, aging test, and heat shock test.

CONCLUSIONS

The synthesis of polyester prepolymers proceeded through the polycondensation of EG, BD, PE, and trifunctional monomers (such as G or TMP) with the dicarboxylic ester, such as DMT, under the optimum condition mentioned above.

Based on the experimental results obtained, temperature, concentration, and catalyst have significant influence on the synthesis of the prepolymer.

The refractive index of the polycondensation system increases markedly, and the reaction time decreases with the increasing monomer concentration in the polymeric system.

Both the Brookfield viscosity and refractive indexes increase with an increase in reaction temperature, and the optimum condition for the system occurs when the reaction takes place at 230°C for 3 h.

The Brookfield viscosity of the 40% w/w solution has been found to increase with a decrease in reactor pressure, and reaches a sustained value as the time under reduced pressure of the system exceeds 40 min.

The presence of the zinc acetate catalyst increases the conversion of the polymeric system. The proper concentration of the catalyst is 1.4×10^{-3} mol % by the DMT.

The deblocking reaction of commercial CT-stable under different temperatures and time was detected from the extent of the regenerated free isocyanate as measured by relative IR absorption intensities. The results indicate that CT-stable deblocking was complete at 210°C for 15 min. The one-component varnishes were prepared by mixing CT-stable with synthesized prepolymers. Through thermogravimetric analysis, these cured varnishes were examined. The TMP modified varnish had a higher temperature at 50% weight loss than that of G.

Testing of magnetic wires, coated with the synthesized varnishes and cured at 210°C for 15 min, indicate that the characteristic properties of the synthesized varnishes were acceptable based on the JIS-2358 Standard Procedure.

The authors wish to express their appreciation to Dr. T. S. Lin, President of the Tatung Institute of Technology, for his support and encouragement.

References

1. K. Iwata, *Polyurethane Resins*, Nikan Industrial News, Tokyo, 1969, Chap. 6, p. 169.
2. J. H. Saunders and K. C. Frisch, *Polyurethane Chemistry and Technology*, Wiley, New York, 1964, Part II, pp. 456-460.
3. D. Singh and S. Ohri, *J. Appl. Polym. Sci.*, **27**, 1191 (1982).
4. I. Goodman, *Encyclopedia of Polymer Science and Technology*, Wiley, New York, 1969, Vol. 11, p. 89.
5. Japanese Standards Association, *Japanese Industrial Standards*, Section Electrical, JIS-C-2358, 1969.
6. W. Griehl and G. Schnock, *J. Polym. Sci.*, **30**, 413 (1958).
7. C. P. Yang and L. T. Lee, *J. Appl. Polym. Sci.*, to appear.
8. N. Kinjo, S. I. Numata, T. Koyama, and T. Narahara, *J. Appl. Polym. Sci.*, **28**, 1729 (1983).

Received December 29, 1986

Accepted August 10, 1987