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Producing Sustainable Unsaturated Polyester for Fiberglass Application

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Abstract. A series of unsaturated polyester resin (UPRs) based on propylene glycol, diethylene glycol, Phthalic anhydride, maleic anhydride with different composition ratio were prepared by polycondensation reaction. Physico-mechanical properties including viscosity, hardness, acid number, gel and peak time are strongly dependent on the content of maleic anhydride in UPR. As increasing the content of maleic anhydride, physico-mechanical properties increased. The obtained UPR was stable for more than 6 months.

INTRODUCTION

Unsaturated polyester resin (UPR) is used for a wide variety of industrial applications including fiberglass, boats, cars, building panels, etc [1-6]. Generally, UPRs result from the condensation reaction between a diprotic acid and a polyhydric alcohol. Diprotic acid part of the polyester I composed of Maleic, fumaric, orthophthalic, isophthalic, and isophthalic acid [3-7]. On the other hand, polyhydric alcohol part is ethylene, propylene, dipropylene, diethylene and neopentyl glycols [5-9]. UPRs are typical high viscosity consisting of polyester resin dissolved in vinyl monomer such as styrene, methyl methacrylate and vinyl toluene. Usually, styrene is common monomer used in UPR to reduce the viscosity of resin and become easier to handle and involved in the curing of the polyester resin through a free radical technique [7-11]. Free radical mechanism of UPR produced by a reaction of peroxide such as benzoyl peroxide (BPO) and methyl ethyl ketone peroxide (MEKP), and accelerators such as N, N dimethyl-p-toluidine (NDPT) and a cobalt salt [11-16]. Rigid material of UPR obtained by the free radical copolymerization between styrene monomer and the polyester double bonds attributed to the cross-linked between resins and styrene. Due to the cross-linking, the resins become gelation, which is a physical change. The cross-linking reaction is an exothermic reaction and temperature increases to 100 – 200 °C [14-16]. A number of researchers have prepared different kinds of UPRs based on different kinds of diacid and glycol to improve the physical and mechanical properties of UPRs [1016].

This article describes the synthesis of UPRs from propylene glycol, diethylene glycol, Phthalic anhydride, maleic anhydride with different composition ratio. The influence of the different of composition of maleic anhydride on physico-mechanical properties of UPR was studied.

EXPERIMENTAL PROCEDURE

Materials. Phthalic anhydride, maleic anhydride, propylene glycol, diethylene glycol, hydroquinone and hydroquinone were obtained from Sigma-Aldrich. Methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate were purchased from Fluka. All the chemical used without purification.

Synthesis of unsaturated polyester resin. A mixture of propylene glycol, diethylene glycol, Phthalic anhydride, maleic anhydride and Xylene as distilling solvent was charged in a four - neck reaction kettle equipped with stirrer, thermometer, nitrogen-gas introducing tube, Dean & Stark apparatus and water condenser. The mixture was mechanically stirred and heated at 140-200 °C under nitrogen gas stream and esterification was carried out while removing water formed by the reaction from the reaction system, continues heating at 140-200 °C . The synthesis was continued until the acid number reached 30 mg / g. After reaching an acid number began to gradually cool the reaction. At the time the resin reached a temperature of 170 ° C, a polymerization inhibitor (hydroquinone) was added. The yield of the resulting unsaturated polyester is 70-72% of the weight of the loaded reactants, which is below the theoretically possible 75%. The reason for this is the loss of phthalic anhydride, which partially sublimates under the conditions of synthesis. The xylene was completely distilled out and reaction

product was allowed to cool. The details about the molar ratio of acids/anhydrides to glycols, styrene monomer and reaction temperature for the synthesis of the unsaturated polyester resins (UPR) are as shown in Table 1.

TABLE 1. Formulation of UPR

| Reactants | Amount (mole) | | | |
|--------------------|---------------|-----|-----|-----|
| | M1 | M 2 | M 3 | M 4 |
| Propylene glycol, | 2.1 | 2.1 | 1.8 | 1.8 |
| Diethylene glycol, | 0.9 | 0.9 | 1.2 | 1.2 |
| Phthalic anhydride | 1.5 | 1.0 | 1.0 | 1.5 |
| Maleic anhydride | 1.5 | 2.0 | 2.0 | 1.5 |
| Styrene | 35% | 35% | 35% | 35% |

The film of the UPR was achieved at room temperature by adding 2 %, by weight of resin, of methyl ethyl ketone peroxide initiator (9% active oxygen) and 0.1%, by weight of resin, of cobalt naphthenate promoter (1.2% solution). Curing was done at room temperature.

RESULTS AND DISCUSSION

The suggested for three-dimensional network structure of curing NPR can be summarized as follows:

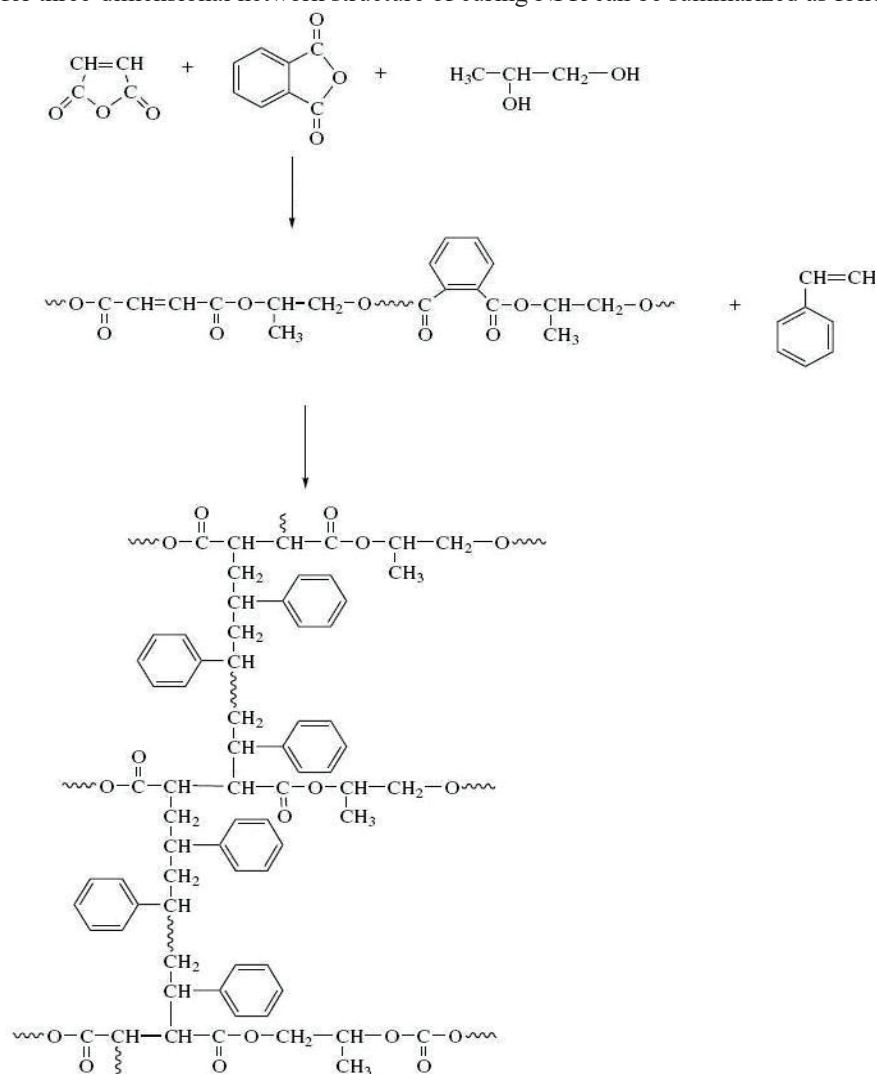


FIGURE 1. Physico -mechanical properties of UPR

Physico-mechanical properties of UPR is shown in Table 2. The solid content of UPR was adjusted to 60% and all measurements were based on 60% solids content. Viscosity is important parameter for UPRs application. For example, low and high viscosities will be sagging and practical difficulty in application. A suitable viscosity is required for application to avoid previous problems. Table 2 shows the increasing in viscosity of UPR with increasing the ratio of maleic anhydride. On the basis of the data obtained, it can be concluded that the gelling time and the peak temperature depend on the chemical composition of the polyester and is directly dependent on the amount of malic anhydride which have an unsaturated bond in the presence of the initiator that reacts with the double bond in styrene and crosslinks the polymer. From Table 2, it can be seen that hardness increased with increasing the amount of maleic anhydride in the UPR due to the increased hard segment contents in the UPR.

TABLE 2. Physico-mechanical properties of the UPR

| Index | M 1 | M 2 | M 3 | M 4 |
|-----------------------------------------------------------------------------|------|------|------|------|
| Density at 20 ° C, g / l | 1.09 | 1.10 | 1.12 | 1.12 |
| Viscosity at 20 ° C according to Brookfield Spindle 2 Speed 50 rmp, dPa * s | 3.1 | 2.7 | 3.6 | 4.2 |
| Solids content, % | 60 | 60 | 60 | 60 |
| Hardness according to Barcol | 38 | 41 | 40 | 37 |
| Gel time, min | 21 | 13 | 14 | 22 |
| Peak time, min | 47 | 27 | 31 | 52 |
| Peak temperature, ° C | 128 | 147 | 151 | 131 |
| Acid number, mgKOH / g | 22 | 24 | 21 | 22 |

The stability of the obtained NPRs during storage in time shown in Table 3. Physico-mechanical characteristics were measured monthly for six months as.

TABLE 3. Specifications of UPR after 6 months.

| Index | M 1 | M 2 | M 3 | M 4 |
|-----------------------------------------------------------------------------|-----|-----|-----|-----|
| Density at 20 ° C, g / l | 1.0 | 1.1 | 1.1 | 1.1 |
| Viscosity at 20 ° C according to Brookfield Spindle 2 Speed 50 rmp, dPa * s | 9 | 0 | 2 | 2 |
| Solids content,% | 3.3 | 2.9 | 3.8 | 4.4 |
| Hardness according to Barcol | 60 | 60 | 60 | 60 |
| Gel time, min | 38 | 41 | 40 | 37 |
| Peak time, min | 24 | 12 | 15 | 24 |
| Peak temperature, ° C | 51 | 29 | 31 | 58 |
| Acid number, mg KOH / g | 128 | 147 | 151 | 131 |
| | 18 | 21 | 19 | 19 |

Comparing the data from Tables 2 and 3, it can be seen that the technical parameter changes are not significant, and the obtained unsaturated polyester resins are able to be stored for a long time without loss of their properties, which is important for the industrial application of UPRs.

The gel time of UPR with different amount of inhibitor is shown in Figure 2.it can be seen that gel time increased with increasing amount of inhibitor (hydroquinone) in UPR. This increase of gel time may be due to the deactivation of double bond in UPR produced by increasing the amount of inhibitor.

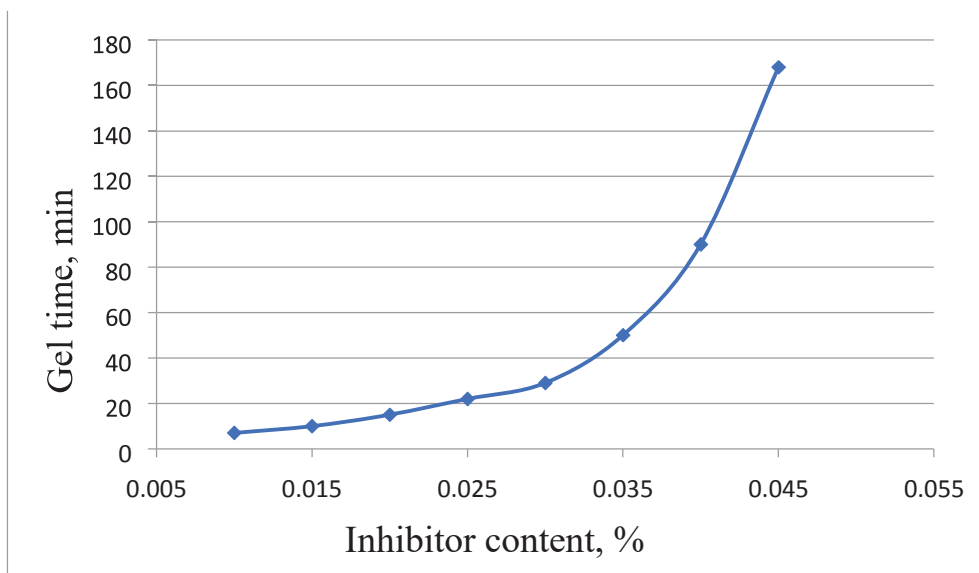


FIGURE 2. The effect of inhibitor content on the gel time of curing UPR.

CONCLUSION

The method for the preparation of unsaturated polyester resins in laboratory conditions was developed and the optimum of polycondensation temperature and ratio of monomer to solvent 65:35 were determined.

On the basis of the data obtained, it can be concluded that the gelling time and the peak temperature depend on the chemical composition of the polyester and is directly dependent on the amount of malic anhydride which have an unsaturated bond in the presence of the initiator that reacts with the double bond in styrene and crosslinks the polymer.

UPR was stable for more than 6 months after preparation at room temperature without loss of their properties, which is important for the industrial application of UPRs.

REFERENCES

1. G. Odian. Principles of Polymerization; 3rd Ed.; John Wiley & Sons; Inc., New York; 53; 1991.
2. B. Parkyn; F. Lamb; and B. V. Clifton; "Polyesters - Unsaturated Polyesters and Polyester Plasticizers" ; Iliffe books Ltd; London; 2; 17; 1967.
3. A. Frodet; and P. Arland; "Unsaturated Polyesters"; Comprehensive Polymer Science; Pergamon Press, New York, Ch. 19, 331; 1989.
4. K. M. England; J. W. Gillespie; W. John, Jr. and B. K. Fink; *J. Compos. Mater.*; 35(15); 1392-1414; 2001.
5. X. Ramis; A. Condinato; J. M. Morancho; J. M. Salla; *Polymer* ; 42(23) ;9469; 2001.
6. M. Nagata and M. Nakae; *J. Polym. Sci.; Part A: Polym. Chem.*; 39(18); 3043; 2001.
7. Y. Howard B.; V. James F. and M. Karen E.; EP 1132429; Eur. Pat. Appl.; 2001.
8. N. T. Qazvini and N. Mohammadi; *Polymer*; 46(21); 9088-9096; 2005.
9. B. Michael A.; and C. Richard.; US 6472069, U.S.; 2002.
10. M. P. Stevens; Polymer Chemistry; 2nd ed.; Oxford University Press. Inc.; 106-120; 1999.
11. M. Avella; R. Dell'erba; E. Martuscelli; R. Partch; *J. Polym. Mater.* ; 17; 445; 2000
12. Y. J. Huang; CH-M. Liang; *Polymer*; 37; 401; 1994
13. S. Y. Pusatcioglu; A. L. Fricke and J. C. Hassler; *J. Appl. Polym. Sci.*; 24; 937; 1979
14. B. K. Kandola; O. R. Horrocks; P. Myler and D. Blair; *Composites Part-A; Applied Science And Manufacturing*; 33A(6); 805-817; 2002.
15. L. B. Manfredi; E. S. Rodriguez; M. W. Przybylak and A. V zquez; *Polymer Degradation and Stability*; 91(2); 255-261; 2006.
16. Kim, J., Jeong, D., Son, C., Lee, Y., Kim, E., Moom, I.: Synthesis & Application of Unsaturated Polyester Resins based on PET Waste, *Korean J. Chem. Eng.*, 24(6), (2007), 1076-1083.