

End-Cap Modified Unsaturated Polyesters With Low Styrene Emission

S Liu¹, J R Chen² and Y Zhang^{1,*}

¹Key Laboratory of Special Functional Polymers and Related Technology of Ministry Education, School of Materials Science and Engineering, East China University of Science and Technology, Meilong Road 130, Shanghai 200237, China

² Shanghai Zhongzhi Chemical Technology Co., Ltd, Nanyangwan Road 1068, Shanghai 201612, China

E-mail: *yzhang@ecust.edu.cn

Abstract. A benzyl end-cap-unsaturated polyester resin (BP-UPR) with low styrene emission was synthesized. The structure of BP-UPR was characterized by Fourier transform infrared (FT-IR) spectroscopy. According to gel permeation chromatography (GPC) measurement, the BP-UPR has a relative low molecular weight ($M_n=1754$) and narrow polydispersity of 1.68. The styrene content of BP-UPR is only 25.1%, 8.3% lower than that of a commercial unsaturated polyester resin (C-UPR) with similar viscosity. The styrene emission of BP-UPR and C-UPR was compared by Luong–Walewski method. At the gel point (17 minutes), the styrene emission of BP-UPR is only 38.9g/m², 15.9% lower than that of C-UPR. After curing for 2 hours, the total styrene emission of BP-UPR is only 62.5 g/m², which is 48.0% lower than that of C-UPR.

1.Introduction

Unsaturated polyester (UP) resins are widely used in the field of fiber reinforced composites because of their good mechanical strength and low costs^[1-2]. And high content of reactive diluents such as styrene are usually used for processing requirement^[3]. However, styrene, as a hazardous air pollutant (HAP) and volatile organic compound (VOC), would emit during spray-up processing and curing reaction and result in severe environment pollution and do great harm to human beings. The legislation of limitation VOC has been put forward by the Federal Environmental Protection Agency of the United States^[4]. And the research on green and low styrene emission (LSE) resins has attracted significant interest.

The volatilization of styrene can be reduced to some extent by adding styrene suppressant additives or replacing styrene with high boiling point diluents. But the weak interlaminar adhesion or poor dilution effect make them have little commercial values^[5-6].

Decreasing the content of styrene dilute in UP resins can reduce styrene emission effectively. Nevertheless, the viscosity of the system may be too high for further processing. The viscosity of the resins mainly depends usually on the molecular weight. By using a monofunctional group monomer to end-cap the growing chains, the precise stoichiometric balance between the reactive acid and alcohol groups would be broken, so the molecular weight of the resins can be controlled effectively. For example, dicyclopentadiene (DCPD) based resin is an end-capped UP resin^[7-8]. However, the poor corrosive resistance and high viscosity attributed to side-reactions of DCPD would limit its application. Low boiling point monohydric alcohols like ethyl alcohol have also been used as the end-capped agent^[9]. But its high evaporation rate results in low efficiency of end-cap reaction.



The synthesis of a new unsaturated polyester with low styrene emission is reported in this paper. Benzyl alcohol (BP), a high boiling point monohydric alcohol, is selected as the end-cap agent. It is much easier to control stoichiometric balance between the reactive groups, and also the molecular weight of the resins. At the same time, the solubility of unsaturated polyester in styrene could also be improved by the replacement of polar carboxyl acid groups with benzyl groups. The structure and the molecular weight of benzyl alcohol end-capped resin (BP-UPR) were analyzed by FT-IR and GPC, respectively. In addition, the styrene emission of BP-UPR and commercial unsaturated polyester resin (C-UPR) during storage and curing reaction are further followed.

2. Experimental

2.1 Reagents.

Maleic anhydride (AR) was obtained from Sinopharm Chemical Reagent Co., Ltd. Isophthalic acid (AR), and neopentyl glycol (AR), propylene glycol (AR), benzyl alcohol (AR) and styrene (AR) were purchased from Shanghai Ling Feng Chemical Reagent Co., Ltd. Commercial unsaturated resin (C-UPR) was provided by Shanghai Zhongzhi Chemical Technology Co., Ltd.

2.2 Measurements.

Fourier transform infrared (FT-IR) spectra was recorded on a Nicolet 5700 spectrometer. The measurement of molecular weight and distribution was performed by a Waters 1515 gel permeation chromatography (GPC). Solid content of the resins was determined according to GB/T 7193-2008. Styrene emission test was performed according to Luong-Walewski^[10] method at room temperature. 60g UP resins were catalyzed by cobalt naphthenate and methyl ethyl ketone peroxide (MEKP) and mixed for one minute. Then 50g catalyzed sample was put uniformly in the watch glass with a diameter of 80mm, then placed in the fume hood immediately and weighed every five minutes. The styrene emission of the resins can be calculated according to the following formula:

$$\text{styrene emission (g/m}^2\text{)} = \frac{\text{weight loss (g)}}{\text{area of lid (m}^2\text{)}}$$

2.3 Synthesis.

Propylene glycol, neopentyl glycol and isophthalic acid were placed in a four-neck flask, and reaction lasted for 4 hours with agitation. Then the maleic anhydride and propylene glycol were added into the flask. The reaction temperature was increased to 200~210°C and the acid value (AV) was tested per hour. The benzyl alcohol was added into the flask at an AV of 140~110mg/g. Keep the reaction until the AV of the system reaches to 7~13mg/g. Then the system was cooled down and styrene was added for dilution.

3. Results and Discussion

3.1 The FT-IR analysis.

A comparison of FT-IR spectra of the obtained end-capped unsaturated polyester resin (BP-UPR) and the unmodified unsaturated polyester is displayed in Figure 1. The IR spectra of two resins shows a series of typical absorption peaks of unsaturated polyester at 1727 cm⁻¹ (C=O group), 2965 cm⁻¹ and 2882 cm⁻¹ (CH₃ group), 1646 cm⁻¹ (C=C group), respectively. Nevertheless, the intensity of the peak at 1727 cm⁻¹ (C=O) for BP-UPR (curve b) is much higher than that of unmodified resin (curve a) by using the peak at 2965 cm⁻¹ (CH₃) as the internal standard. It demonstrates the esterification reaction between the benzyl alcohol and carboxyl groups at the terminal of UP molecular chains. Furthermore, a new absorption band at 701 cm⁻¹ corresponding to the C-H flexural of mono-substituted benzene derivatives appears, indicating that the unsaturated polyesters are end-capped by benzyl alcohol.

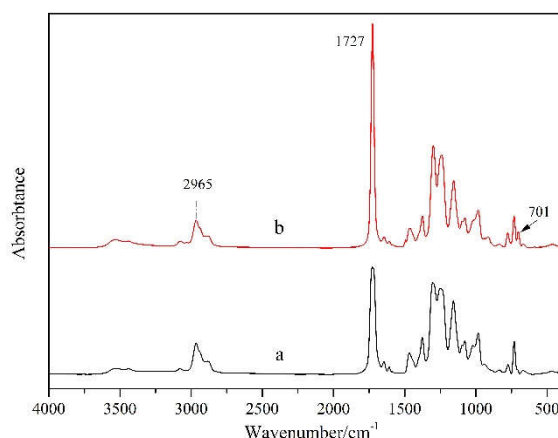


Figure 1. FT-IR spectra of the unmodified unsaturated polyester resin (a) and the BP-UPR (b).

3.2 Molecular weight of BP-UPR.

The GPC spectra of BP-UPR and commercial resin (C-UPR) are compared in Figure 2. The molecular weight as well as its distribution, styrene content of BP-UPR and C-UPR are shown in Table 1. It can be seen that the molecular weight (M_n and M_w) of BP-UPR is much lower than that of C-UPR because the end-capped reaction of benzyl alcohol has broken the precise stoichiometric balance between reactive acid and alcohol groups. The lower molecular weight of the resins implies lower viscosity of system, so that less diluent (styrene) is needed for processing. The styrene content of BP-UPR is only 25.1%, which is 8.3% lower than that of C-UPR with the same viscosity (1150cp). It means that styrene emission of BP-UPR is much lower than that of C-UPR during storage and shipping.

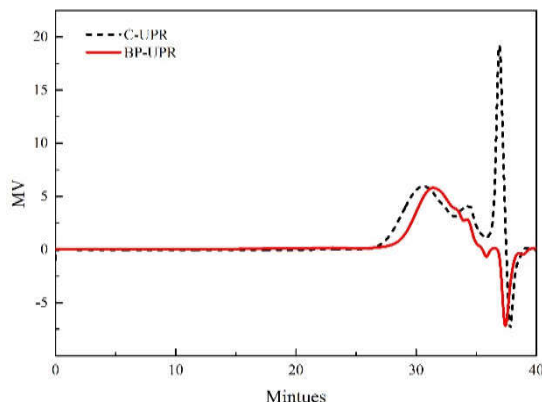


Figure 2. GPC curves of C-UPR and BP-UPR.

Table 1. Molecular weight and distribution and styrene content of C-UPR and BP-UPR.

	M_n	M_w	PDI	Styrene content/%
C-UPR	3204	5287	1.65	33.4
BP-UPR	1754	3558	1.68	25.1

3.3 Styrene emission.

A further comparison of styrene emission in curing stage of BP-UPR and C-UPR is shown in Figure 3. At first, the volatilization of styrene in two resins tends to increase with the time linearly because the low viscosity and high styrene diffusivity allow styrene to reach the resin's surface freely^[11]. Therefore, the initial emission rate only depends on the styrene content of resins. Due to the low styrene content of BP-UPR (25.1%), its styrene volatilization before gel is only 38.9g/m², which is 15.9% lower than that of C-UPR. After curing reaction lasted for 17 minutes, the resins began to gel and the

three-dimensional net structure was gradually formed. At the same time, the viscosity of the system increased sharply, so the styrene emission rate slowed down. One hour later, there is no styrene emission for BP-UPR while some emission still existed for C-UPR because it has a higher styrene content. More styrene monomers were trapped in the three-dimensional net structure of the cured resins. It would take more time for residual styrene monomers to be completely released. After 2 hours, there was hardly any styrene emission for both C-UPR and BP-UPR. The total styrene emission of BP-UPR is only 62.5 g/m^2 , which is 48.0% lower than that of C-UPR.

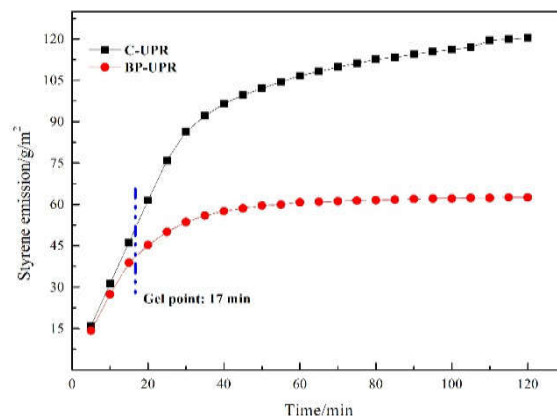


Figure 3. Styrene emission of BP-UPR and C-UPR in curing stage.

4. Conclusions

- (1) A benzyl end-capped unsaturated resin (BP-UPR) was synthesized by using benzyl alcohol as the end-capper. FT-IR analysis demonstrates its structure.
- (2) Compared with the commercial unsaturated polyester (C-UPR), BP-UPR has a lower molecular weight ($M_n=1754$) and a similar polydispersity ($PDI=1.68$). The styrene content of BP-UPR is only 25.1%, which is 8.3% lower than that of C-UPR with same viscosity (1150cp).
- (3) At the first stage of curing reaction, styrene volatilization of two UP resins tends to increase with the time linearly. The volatilization amount of BP-UPR before gel was 38.9 g/m^2 , 15.9% lower than that of C-UPR. After gel, the styrene emission rate of the two resins began to slow down. After curing reaction lasted for 2 hours, the total styrene emission of BP-UPR was only 62.5 g/m^2 , which is 48.0% lower than that of C-UPR.

5. References

- [1] Fonseca A C, Costa C S M F, Marques T M P, Coelho J F J and Serra A C 2017 *J. Mater. Sci.* **52** 1272-84
- [2] Nguyen Q T, Ngo T D, Bai Y and Tran P 2016 *Fire Mater.* **40** 1047-69
- [3] Erdem A and Kusefoglu S 2011 *242nd National Meeting of the American-Chemical-Society* (Denver: Colorado)
- [4] Perrot Y, Davies P, Keboul A and Baley C 2008 *Appl. Compos. Mater.* **15** 87-97
- [5] Jaswal S and Gaur B 2015 *Green Proc. and Synth.* **4** 191-202
- [6] Youngblood J P, Sellars A B, Clark A J and Coles S R 2015 *Green Mater.* **3** 35-42
- [7] Maurin R, Perrot Y, Bourmaud A, Davies P and Baley C 2009 *Composites Part A* **40** 1024-32
- [8] Chengguo L, Wen L, Zhengchun C, Jianqiang C, Lihong, Yan D and Yonghong Z 2013 *Ind. Crops. Prod.* **49** 412-18
- [9] Loza R and Hartinger D G 2004 US 6794483 B2[P]
- [10] Raul D 2000 *Reinf. Plast.* **44** 42-44
- [11] Scala J J, Orlicki J A, Jain R, Ulven C A, Palmese G R, Vaidya U K and Sands J M 2009 *Clean Technol. Environ. Policy* **11** 283-92