

Effect of Succinic Acid on the Shrinkage of Unsaturated Polyester Resin

Cheng-Ming Hong,¹ Xiao-Jun Wang,¹ Peng Kong,¹ Zhi-Gang Pan,¹ Xiao-Yao Wang²

¹College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, Peoples Republic of China

²The Charles E. Via, Jr. Department of Civil and Environmental Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA

Correspondence to: X.-J. Wang (E-mail: xjwang@njtech.edu.cn)

ABSTRACT: Succinic acid was presented as a small molecule low shrinkage additive (LSA) in unsaturated polyester resin (UPR). The effects of succinic acid on the volume shrinkage and the flexural strength of UPR cured at $80 \pm 1^\circ\text{C}$ were investigated and compared with those of macromolecule LSAs, including polyvinyl acetate (PVAc), polymethyl methacrylate (PMMA), and polystyrene (PS). The results indicated that the volume shrinkage of succinic acid/UPR specimen was significantly lower than those of specimens with macromolecule LSAs. The flexural strength of succinic acid/UPR specimen was improved. The optimal time of pre-esterification between succinic acid and the excess dihydric alcohol in UPR was 3.0 h, and the optimal addition of succinic acid was 20 g per 100 g UPR. Compared with 2,2-dimethyl malonic acid we put forward before, succinic acid was a cheaper and more commercial LSA, which obviously accelerated the pre-esterification process and presented excellent antishrinkage effect. DSC showed that with the addition of succinic acid, the polymerization of UPR was distinctive. The two-stage polymerization of UPR glue including the cross-polymerization of UPR and the homopolymerization of polyester was changed to a one-stage polymerization with lower exotherm and slower polymerization rate, which was optimal for UPR. FTIR and high resolution magic angle spinning nuclear magnetic resonance (HR/MAS NMR) were applied for the quantitative characterization of pre-esterification caused by succinic acid. Succinic acid performed better effects on the polymerization of UPR as compared to previous LSAs, and finally the homogeneous micro-structure of cured succinic acid/UPR formed and was demonstrated by SEM. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41276.

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INTRODUCTION

Unsaturated polyester resin (UPR) and the composite materials based on UPR are widely used in automotive component, electrical engineering, and chemical industries for their easy processing, excellent mechanical properties, good aging, anticorrosion as well as electric insulation. Antishrinkage is critical to the UPR and the composite materials of UPR matrix. During the curing process of the UPR, the cross-polymerization and the internal stress caused by the violent heat release result in cracks, micro voids and severe volume shrinkage from 7 to 10% for the cured UPR. The volume shrinkage leads to problems of severe surface quality and dimensional control in the manufacture of cured UPR and the composite materials of UPR matrix.^{1–3}

At present, low shrinkage additive (LSA) is commercially applied to compensate the volume shrinkage of UPR during the curing process by taking the advantage of thermal expansion and micro voids caused by LSA. The LSA can be divided into

polar LSA, weak polar LSA and nonpolar LSA, and polar LSA exhibits the most efficient antishrinkage effect among them.^{4,5} The previous researches showed that in the application of polar LSA, the small temperature gradient in the curing process caused insufficient thermal expansion, and the mechanical properties of the composite materials were deteriorated.^{6–8}

Our research group presented 2,2-dimethyl malonic acid as a small molecule LSA in UPR/ CaCO_3 composite specimen.⁹ A novel pre-esterification mechanism was proposed between 2,2-dimethyl malonic acid and the excess dihydric alcohol in UPR to form esterifiable macromolecular compounds, which performed restraint on the cross-polymerization of UPR and resulted in lower shrinkage of specimen. However, as one kind of pharmaceutical intermediates, 2,2-dimethyl malonic acid was expensive and the pre-esterification caused by 2,2-dimethyl malonic acid lasted as long as 48 h. These two properties were disadvantageous to the industrial application.

As a cheaper and more commercially available product, succinic acid was widely used. The global production of succinic acid is 30,000 to 50,000 tonnes per year and the market price of succinic acid is \$6,000–9,000 per tonne, about 80% cheaper than 2,2-dimethyl malonic acid.^{10,11} Succinic acid made a better contribution to electrophilicity of its carboxy group than that of 2,2-dimethyl malonic acid.¹² Succinic acid was able to react with dihydric alcohol more rapidly to form esterifiable macromolecular compound and to restrain the cross-polymerization of UPR. The restraint of cross-polymerization of UPR was conducive for the low shrinkage of cured UPR.^{13,14} Therefore, succinic acid was applied as an LSA in the study, and its novel antishrinkage effect on UPR was discussed.

In addition to controlling the volume shrinkage of the UPR, the optimal polymerization of UPR may be realized with the addition of succinic acid. During the curing process of the UPR, cross-polymerization of UPR and homopolymerization of polyester proceeded, respectively. An optimal polymerization of UPR was the cross-polymerization between polyester and styrene, while the homopolymerization of polyester alone was eliminated. This kind of polymerization could form the optimal three-dimensional structure in UPR curing, and could decrease the volume shrinkage and increase the strength of cured UPR.^{15,16} Therefore, in this work, the optimization of the polymerization of UPR during the curing process as well as the shrinkage control of cured UPR with the presence of the small molecule LSA was investigated. This novel proposition might be beneficial for the UPR polymerization in the future.

EXPERIMENTAL

Materials

The UPR used in this work was an orthophthalic polyester resin obtained from Jinling DSM Resins, in China. The initiator was a commercial product from Akzo Nobel N.V containing more than 33 wt % methyl ethyl ketone peroxide. The promoter used in this study was cobalt naphthenate containing about 1 wt % cobalt from Akzo Nobel N.V. The small molecule LSA used in this work was succinic acid produced by Jiangsu Yonghua Fine Chemical, in China, containing more than 99.5 wt % succinic acid. The macromolecule LSAs used in this study were PVAc, PMMA, and PS obtained from Jinling DSM Resins, in China.

Preparation of the Specimens

All the cured UPR specimens were prepared according to ISO 3672-2:2000 as well as the references,^{17,18} and the formulation was set as 100 g resin : 1 g initiator : 0.5 g promoter. The mass ratio of LSA used in production is usually more than 30 g per 100 g UPR.^{19,20} In the experiment, the additions of LSAs were set at 5 g, 10 g, 15 g, 20 g, 25 g, and 30 g to control the content of LSAs within 30 g per 100 g UPR and to weaken the influences of LSAs on the properties of cured UPR.

The UPR glue and succinic acid in a specific ratio pre-esterified under stirring at 200 rpm at $25 \pm 2^\circ\text{C}$ in a beaker firstly. The pre-esterification time was set at 0.5 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, 3.0 h, and 3.5 h, respectively. A long pre-esterification time was set at 48.0 h in order to compare with the volume shrinkage change in the Ref. 9, and reconfirm the

change tendency of shrinkage after the long pre-esterification time. After that, 0.5% promoter by the mass ratio of UPR was added into the beaker and stirred, and finally, 1.0% initiator by the mass ratio of UPR was added and stirred uniformly. The cured UPR specimens with the dimension of $120 \times 15 \times 6 \text{ mm}^3$ were prepared according to the international ISO 3672-2:2000.

Property Testing

The volume shrinkage of the cured UPR specimens was measured according to the international ISO 3521-1997 “Plastics—Unsaturated Polyester and Epoxy Resins—Determination of Overall Volume Shrinkage” at the temperature of $23 \pm 0.1^\circ\text{C}$. The flexural strength was measured by three-point bending tests with electronic universal testing machine CMT 5254 (made by Shenzhen SANS Measurement Technology, in China with the maximum flexural force of 100 kN and the accuracy of 0.5%), according to the international ISO 2602 “Test Methods for Properties of Resin Casting Body” at the ambient temperature of $23 \pm 2^\circ\text{C}$ and relative humidity of $50 \pm 5\%$. In the parallel experiment, five replicated specimens were tested for each formulation and the experiment was repeatable.

Fourier Transform Infrared (FTIR) Spectroscopy

The pre-esterification between succinic acid and the excess dihydric alcohol in UPR glue was qualitatively characterized by an FTIR spectrometer (Nicolet Nexus670) with a resolution of 2 cm^{-1} . After the pre-esterification, a liquid film of the glue specimen was coated on the KBr plate, which was less than 2 mm in thickness. Ten scans from 4000 cm^{-1} to 400 cm^{-1} were taken for each specimen.

Differential Scanning Calorimetry (DSC)

An instrument NETZSCH DSC204 DSC was used for measuring the polymerization process of UPR glue specimens. The specimens were sealed in a volatile aluminum sample pan. Nonisothermal scans were carried out from 30 to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$ under the nitrogen atmosphere. The modulation of temperature for DSC was $\pm 0.1^\circ\text{C}$. The mass of UPR glue specimens in the experiment was 3–7 mg and the sensitivity of the DSC was $0.1 \mu\text{g}$.

High Resolution Magic Angle Spinning Nuclear Magnetic Resonance (HR/MAS NMR)

^1H high resolution magic angle spinning nuclear magnetic resonance (HR/MAS NMR) spectrum was obtained by a Bruker AVANCE 400 MHz (9.40T) NMR equipped with 4 mm/15 kHz HR/MAS probe for the quantitative analysis of pre-esterification and the residual succinic acid in UPR. The cured UPR specimen was ground into particle of 0.1 mm, and then the accurately weighed 10.0 mg sample was inserted into 4 mm HR/MAS-NMR ZrO_2 rotor. Deuterium oxide was used as a deuterium solvent. ^1H HR/MAS-NMR spectrum was acquired by spinning the sample at 4 kHz.

Scanning Electron Microscopy (SEM)

The cured UPR specimens were cut into the size of $5 \times 5 \times 2 \text{ mm}^3$. The sections of the samples were observed by using a SEM (JEOL JSM-6510) with 10 kV accelerating voltage in high vacuum mode and a magnification of $2000\times$, in order to

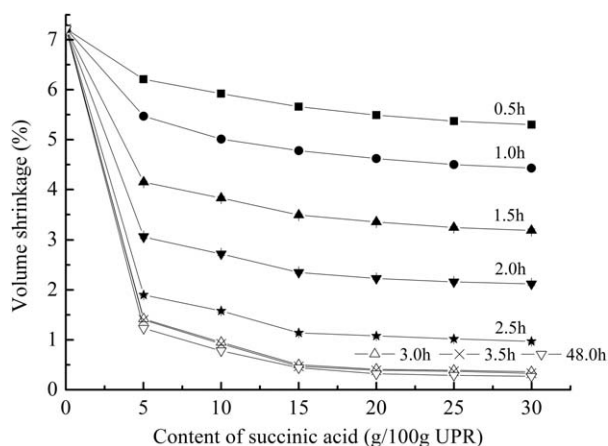


Figure 1. The volume shrinkage of succinic acid/UPR specimens at different pre-esterification time.

investigate the micro morphology of the samples. The section surfaces were sputtered with a thin gold layer to enhance electronic conductivity.

RESULTS AND DISCUSSION

The Effects of Pre-Esterification Time and the Content of Succinic Acid on the Volume Shrinkage of Succinic Acid/UPR Specimen

The relations between the volume shrinkage of succinic acid/UPR specimen and pre-esterification time as well as the content of succinic acid are shown in Figure 1. Figure 1 shows that the initial volume shrinkage of the cured UPR specimen without LSA is $7.22 \pm 0.02\%$, and later, the volume shrinkage of succinic acid/UPR specimen decreases with the prolongation of pre-esterification time. With the content of 30 g succinic acid per 100 g UPR, the volume shrinkage of succinic acid/UPR specimen decreases to $5.30 \pm 0.02\%$ and $0.36 \pm 0.02\%$, corresponding to the pre-esterification time of 0.5 and 3.0 h. Furthermore, the volume shrinkage of succinic acid/UPR specimens are $0.33 \pm 0.02\%$ and $0.27 \pm 0.01\%$, corresponding to the pre-esterification time of 3.5 and 48.0 h, implying no more appa-

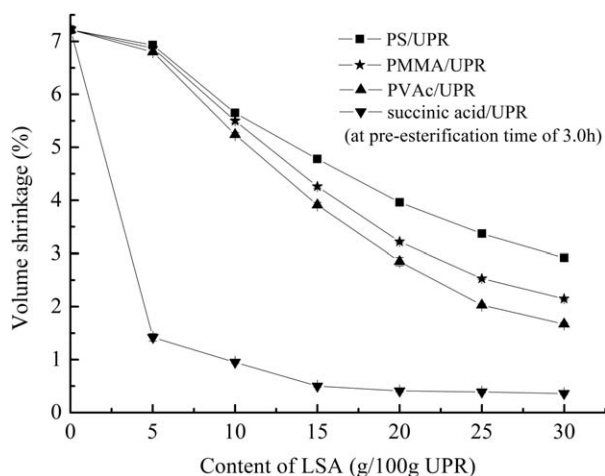


Figure 2. The volume shrinkage of UPR specimens with succinic acid and three different polarities macromolecule LSAs.

rent decrease of shrinkage after 3.0 h pre-esterification. It is illustrated that the excess dihydric alcohol in UPR was completely consumed by succinic acid through 3.0 h pre-esterification, and the shrinkage of succinic acid/UPR specimen became stable. As a result, prolongation of the pre-esterification time was ineffective to shrinkage, and the optimal pre-esterification time of succinic acid/UPR system was set at 3.0 h in this experiment. The pre-esterification time of succinic acid/UPR specimen (3.0 h) was much shorter than that of 2,2-dimethyl malonic acid/UPR specimen (48.0 h), and was beneficial to industrial application.

Figure 1 also shows that the volume shrinkage of succinic acid/UPR specimen decreases with the increasing addition of succinic acid. As for the addition of succinic acid less than 15 g per 100 g UPR, the volume shrinkage of succinic acid/UPR specimen presents a significant decrease because of the high content of excess dihydric alcohol in the initial reaction.^{21,22} Later, the change of the volume shrinkage of succinic acid/UPR specimen becomes gentle. When the addition of succinic acid is over 20 g per 100 g UPR, the volume shrinkage of succinic acid/UPR specimen reaches $0.41 \pm 0.02\%$ at the pre-esterification time of 3.0 h. It indicates that at the pre-esterification time of 3.0 h, the proper addition of succinic acid is 20 g per 100 g UPR.

Figure 2 illustrates the antishrinkage effect of succinic acid and macromolecule LSAs of three different polarities on UPR. The results show that the volume shrinkage of cured UPR with polar LSA PVAc is lower than those of cured UPR with weak polar LSA PMMA and nonpolar LSA PS. Under the condition of the pre-esterification time of 3.0 h and the content of 5 g succinic acid per 100 g UPR, the antishrinkage effect of succinic acid is more apparent than that of the macromolecule LSAs as shown in Figure 2. The volume shrinkage of succinic acid/UPR specimen is $1.42 \pm 0.07\%$ and those of macromolecule LSAs/UPR specimens are about 7.00%. Meanwhile, as of the addition of 30 g LSA per 100 g UPR, the volume shrinkage of PVAc/UPR specimen reaches $1.67 \pm 0.03\%$, but the volume shrinkage of succinic acid/UPR specimen is only $0.36 \pm 0.02\%$. It could be summarized that succinic acid was a low cost LSA with an excellent antishrinkage effect on UPR.

The Effects of Pre-Esterification Time and the Content of Succinic Acid on the Flexural Strength of Succinic Acid/UPR Specimen

The relations between the flexural strength of succinic acid/UPR specimen and the pre-esterification time as well as the content of succinic acid are shown in Figure 3. Figure 3 shows that in the range of 5–15 g succinic acid per 100 g UPR, the flexural strength of succinic acid/UPR specimen at pre-esterification time of 3.0 h is lower than those of 2.0 h and 1.0 h. In the range of 20–30 g succinic acid per 100 g UPR, the flexural strength of succinic acid/UPR specimen at pre-esterification time of 3.0 h is higher than those of 2.0 and 1.0 h. With great emphasis on the shrinkage, the shrinkage at the pre-esterification time shorter than 3.0 h is above 0.50%. Therefore, considering the effect of pre-esterification time on the volume

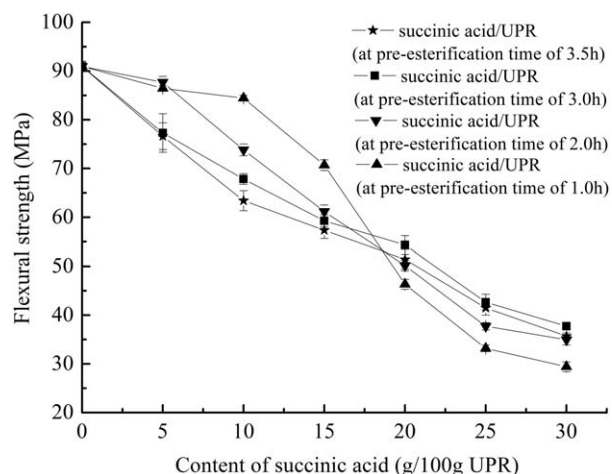


Figure 3. The flexural strength of succinic acid/UPR specimens at different pre-esterification time.

shrinkage of succinic acid/UPR specimen, the optimal pre-esterification time is reconfirmed at 3.0 h.

The experimental result in the first section above revealed that, under the condition of the pre-esterification time of 3.0 h, the volume shrinkage of succinic acid/UPR specimen is below 0.50% as the addition of succinic acid is 20–30 g per 100 g UPR. Considering the change of the flexural strength of succinic acid/UPR specimen and the effect of the content of succinic acid on the flexural strength, the addition of succinic acid is reconfirmed as 20 g per 100 g UPR corresponding to the pre-esterification time of 3.0 h. The flexural strength under this condition is 54.33 ± 1.90 MPa shown in Figure 2, much higher than those of 25 and 30 g succinic acid per 100 g UPR specimens at the same pre-esterification time.

Compared with the macromolecule LSAs, less succinic acid is required to achieve the same level of volume shrinkage as shown in Figure 4. The flexural strength of succinic acid/UPR specimen at the pre-esterification time of 3.0 h is 54.33 ± 1.90

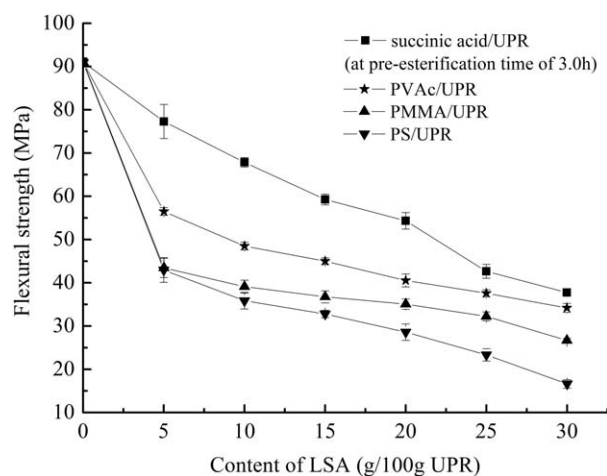


Figure 4. The flexural strength of UPR specimens with succinic acid and three different polarities macromolecule LSAs.

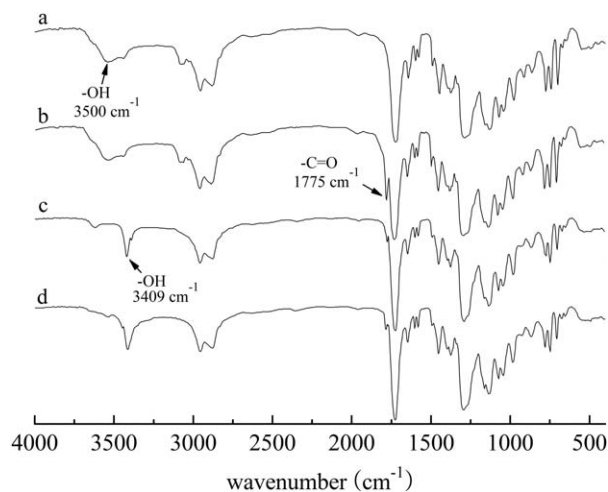


Figure 5. The FTIR spectra of (a) the UPR glue, (b) the succinic acid/UPR glue before pre-esterification, (c) and (d) the succinic acid/UPR glue at pre-esterification time of 3.0 and 48.0 h.

MPa, higher than those specimens with different kinds of macromolecule LSAs at 40.54 ± 1.50 MPa (PVAc/UPR), 35.06 ± 1.20 MPa (PMMA/UPR), and 28.59 ± 1.89 MPa (PS/UPR), respectively.

Fourier Transform Infrared (FTIR) Spectroscopy Experiment

The FTIR characterization was done for UPR glue and succinic acid/UPR glue specimens at different pre-esterification time to analyze the reaction between succinic acid and the excess diglycidic alcohol in UPR glue qualitatively. The FTIR spectra are shown in Figure 5.

The spectra illustrate that the stretching vibration of the alcoholic hydroxyl group (R—OH) appears at the wavenumber of 3500 cm^{-1} ^{23,24} for UPR glue and succinic acid/UPR glue specimens before pre-esterification, indicating the existence of dihydric alcohol in the UPR and in the succinic acid/UPR glue.

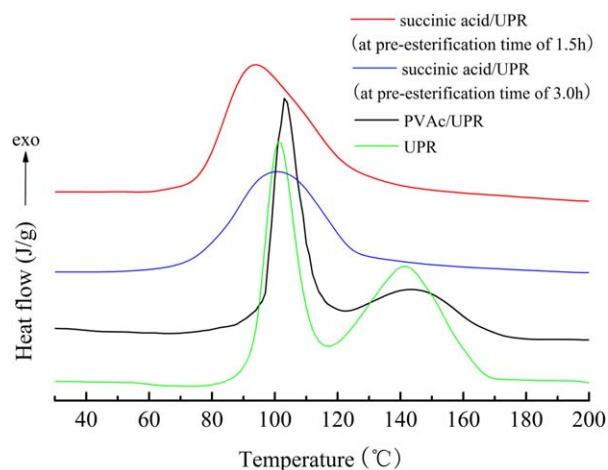


Figure 6. The DSC thermogram of the UPR, the UPR with succinic acid and with PVAc in the content of 20 g per 100 g UPR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Thermal Properties of the UPR, PVAc/UPR, and Succinic Acid/UPR

Specimen	Cross-polymerization peak		Self-polymerization peak	
	Peak width (temperature range) (°C)	Reaction exotherm ΔH (J·g ⁻¹)	Peak width (temperature range) (°C)	Reaction exotherm ΔH (J·g ⁻¹)
UPR	17.1 (93.3–110.4)	159.0	43.9 (121.3–165.2)	158.6
PVAc/UPR	24.7 (92.5–117.2)	155.6	38.1 (123.5–161.6)	115.8
Succinic acid /UPR (at pre-esterification time of 1.5 h)	43.5 (75.7–119.2)	154.3	-	-
Succinic acid/UPR (at pre-esterification time of 3.0 h)	57.3 (67.7–125.0)	116.7	-	-

After 3.0 h pre-esterification, the intensity of the corresponding absorption of the hydroxyl group weakens significantly for the succinic acid/UPR glue specimens, illustrating the consumption of the alcoholic hydroxyl group. The absorption of the carbonyl group of carboxyl in succinic acid at the wavenumber of 1775 cm⁻¹^{23,24} weakens. It means that the carbonyl group of carboxyl in succinic acid changed to the carbonyl group of ester through the pre-esterification. In the meantime, a typical characteristic absorption for the stretching vibration of the hydroxyl group in aqua appears at the wavenumber of 3409 cm⁻¹.^{23,24} It demonstrated that the pre-esterification proceeded and the aqua generated.

Differential Scanning Calorimetry (DSC) Experiment

Among the three kinds of macromolecule LSAs, the polar LSA of PVAc performed the best antishrinkage efficiency for its good compatibility with UPR. Therefore, the innovation of succinic acid to UPR was introduced and compared with that of PVAc in the study. The DSC experiment was conducted for the UPR glue specimens with succinic acid and PVAc at the content of 20 g per 100 g UPR, exploring the difference of polymerization of UPR between these two LSAs. The DSC thermogram is shown in Figure 6.

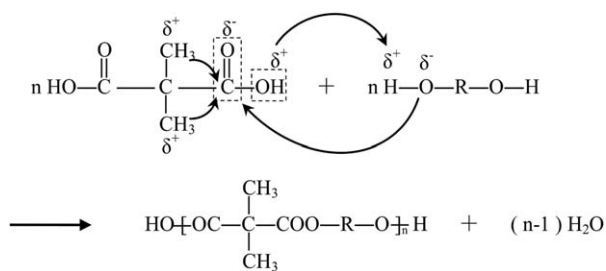
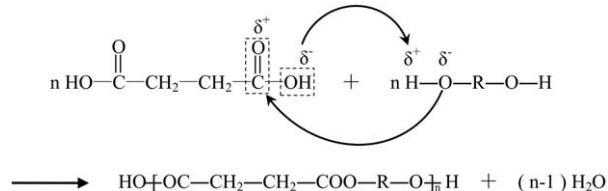
Figure 6 shows that there are two exothermic peaks for UPR and PVAc/UPR specimens. However, only one wide exothermic peak arises for succinic acid/UPR specimen, which is different from the previous curing process of UPR and different from that of 2,2-dimethyl malonic acid/UPR/CaCO₃ specimen in the Ref. 9. The thermal properties of the UPR, PVAc/UPR and succinic acid/UPR (at pre-esterification time

of 1.5 and 3.0 h) taken from the first DSC scan are listed in Table I.

The previous researches of the curing process of the UPR by nonisothermal DSC scan showed that the double reaction peaks or peaks with shoulders usually appeared in the DSC curve. The first exothermic peak was corresponding to the crosslinking reaction between styrene and polyester molecules, and the second one was associated to the homopolymerization of polyester itself.^{25,26} The polyester molecules would cross-polymerize with styrene firstly at about 100°C owing to the low activation energy. At higher temperatures over 140°C, polyester coils possessed enough energy to override steric hindrances and the polyester homopolymerization became notable.²⁷ In the experiment, with the presence of succinic acid, the single exothermic peak (appearing at about 100°C) could be attributed to the crosslinking between polyester and styrene.

On the basis of the research results of Pucić and Ranogajec, Avella et al., and Monti et al.,^{25–27} the unique exothermic peak of the succinic acid/UPR specimen without the homopolymerization of polyester could be assigned to an optimal polymerization of UPR. The optimal polymerization process was different from those of conventional polymerization of the UPR and 2,2-dimethyl malonic acid/UPR/CaCO₃ specimen, where the homopolymerization of polyester was not eliminated and was adverse to the shrinkage of the specimen.

The difference of polymerization between the specimen with 2,2-dimethyl malonic acid and the specimen with succinic acid was attributed to the difference of pre-esterification. The formation of aqua and thermoplastic polyester in the different pre-esterification processes is described in Figures 7 and 8, corresponding to the presence of 2,2-dimethyl malonic acid and

**Figure 7.** The pre-esterification process between 2,2-dimethyl malonic acid and dihydric alcohol in UPR.**Figure 8.** The pre-esterification process between succinic acid and dihydric alcohol in UPR.

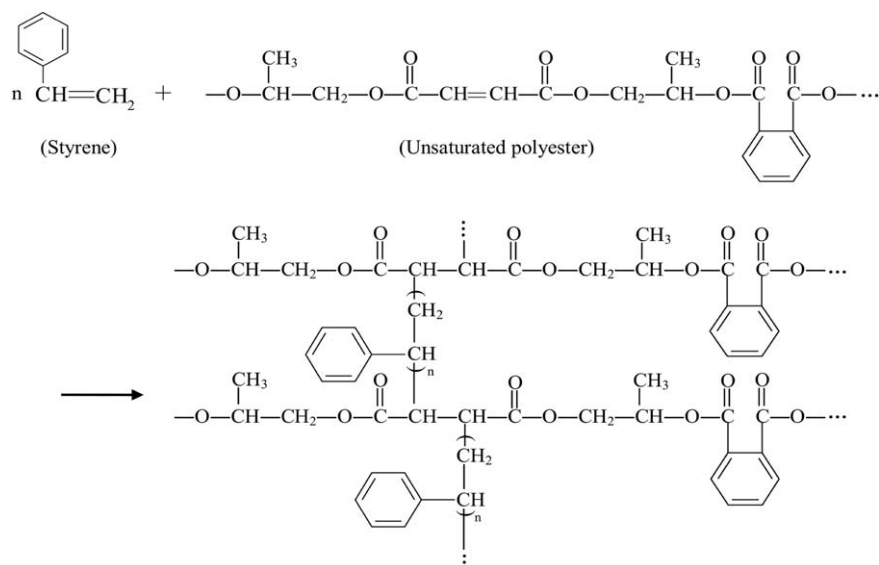


Figure 9. The optimal polymerization of succinic acid/UPR specimen.

succinic acid. The molecular structure of succinic acid was different from that of 2,2-dimethyl malonic acid with two symmetrical methyl substituent groups at the alpha carbon atom. The two symmetrical methyl substituent groups produced two effects of electron donating and space steric, which did not exist in succinic acid. Therefore, the nucleophilic attack from dihydric alcohol to the carbon atom in carboxy group was hindered, and the pre-esterification between 2,2-dimethyl malonic acid and dihydric alcohol was slowed down.

Comparing with the FTIR spectra of 2,2-dimethyl malonic acid in the Ref. 9, more aqua was acquired with the presence of succinic acid at the same pre-esterification time (Figure 5). The aqua produced by the pre-esterification between succinic acid and dihydric alcohol restrained the initiation of free radicals,²⁸ and slowed down the cross-polymerization rate of

UPR. Additionally, more aqua hindered the cross-polymerization of UPR efficiently. It was possible for polyester to crosslink with styrene thoroughly, and meanwhile, the homopolymerization of polyester was eliminated. These two changes were conducive to decrease the structural shrinkage. Finally, the optimal polymerization of UPR with lower exotherm, slower polymerization rate and without polyester homopolymerization was completed. It was evident that succinic acid performed better effects on UPR as compared with 2,2-dimethyl malonic acid.

On the basis of the pre-esterification, the optimal cross-polymerization between polyester and styrene as well as the formation of three-dimensional structure in succinic acid/UPR specimen are illustrated in Figure 9.

Table I shows that the temperature ranges of cross-polymerization for the succinic acid/UPR specimens are from 75.7 to 119.2°C and from 67.7 to 125.0°C corresponding to 1.5 and 3.0 h pre-esterification time. Together with the DSC thermogram in Figure 6, it can be deduced that due to the wide and high exothermic peak of the cross-polymerization, the small exothermic peak of pre-esterification between succinic acid and the excess dihydric alcohol in UPR is buried at the temperature of 110°C.

The total reaction exotherm of the UPR is 317.6 J g⁻¹ and that of PVAc/UPR is 271.4 J g⁻¹ as shown in Table I. Nevertheless, for the succinic acid/UPR at pre-esterification time of 1.5 and 3.0 h, the total reaction exotherm is 154.3 and 116.7 J g⁻¹, respectively. Obviously, the total reaction exotherm of UPR with succinic acid is much lower than those of UPR and UPR with PVAc, which indicates a lower degree of cross-polymerization. As for the prolongation of pre-esterification time from 1.5 to 3.0 h for succinic acid/UPR specimen, the decrease of the total reaction exotherm reconfirmed that the 3.0 h pre-esterification time corresponded to a lower degree of

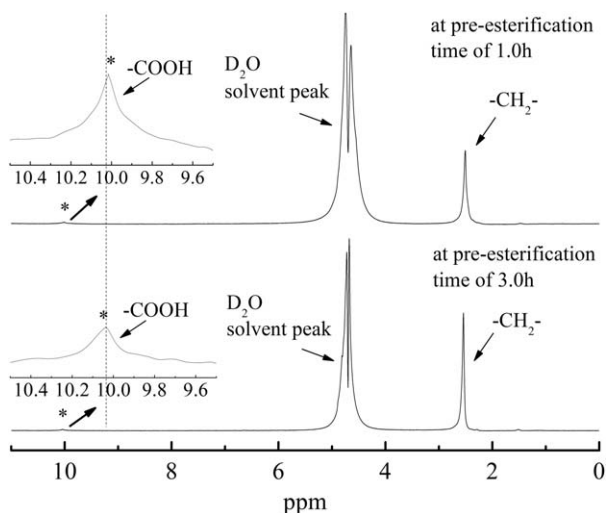


Figure 10. ¹H HR/MAS-NMR spectra of the cured succinic acid/UPR specimens at different pre-esterification time.

Table II. Experimental ^1H HR/MAS-NMR Chemical Shift, Assignment and Integral

Specimen	Chemical shift δ (ppm)	Assignment	Integral
Succinic acid	2.50	$-\text{CH}_2-$	1.000
	12.17	$-\text{COOH}$	0.046
Succinic acid/UPR (at pre-esterification time of 1.0 h)	2.51	$-\text{CH}_2-$	1.000
	10.02	$-\text{COOH}$	0.037
Succinic acid/UPR (at pre-esterification time of 3.0 h)	2.54	$-\text{CH}_2-$	1.000
	10.04	$-\text{COOH}$	0.016

cross-polymerization as well as the lower volume shrinkage of the succinic acid/UPR specimen.

Table I also indicates that the cross-polymerization time of UPR is 1.71 min ($17.1^\circ\text{C}/(10^\circ\text{C min}^{-1}) = 1.71$ min) at the heating rate of $10^\circ\text{C min}^{-1}$. The corresponding cross-polymerization time of succinic acid/UPR specimen at the pre-esterification time of 1.5 and 3.0 h is 4.35 min ($43.5^\circ\text{C}/(10^\circ\text{C min}^{-1}) = 4.35$ min) and 5.73 min ($57.3^\circ\text{C}/(10^\circ\text{C min}^{-1}) = 5.73$ min), respectively. Therefore, the cross-polymerization time of UPR was prolonged significantly with the addition of succinic acid and the prolongation of the pre-esterification time. The slower cross-polymerization rate was conducive to release the internal stress, to decrease the cracks and micro voids, as well as to lower the volume shrinkage of the succinic acid/UPR specimen.

In summary, the unique exothermic peak, lower polymerization exotherm, and prolongation of cross-polymerization time led to the specific curing process of UPR with the presence of succinic acid. The lower volume shrinkage and higher flexural strength could be obtained from the specific and the optimal curing process of UPR.

High Resolution Magic Angle Spinning Nuclear Magnetic Resonance (HR/MAS-NMR) Experiment

In the analysis of DSC, the exothermic peak of pre-esterification caused by succinic acid was deduced to be buried by the wide exothermic peak of polymerization of UPR. To investigate and characterize the pre-esterification caused by succinic acid, HR/MAS-NMR was applied as an innovation for the quantitative analysis of pre-esterification.

It is difficult for the cured succinic acid/UPR specimen to dissolve in the deuterated solvent. The solid-state ^1H NMR spectra usually exhibit a wide peak, which is not available for the quantitative analysis. Therefore, the residual succinic acid in the cured specimen is difficult to detect by solution NMR and solid-state NMR. HR/MAS NMR, which is commonly applied in the semi-solid state specimens, can be extended to the solid specimens^{29,30} and be able to get the sharp peaks of small molecule in solid specimens or the branched structure of the macromolecule. Accordingly, the residual succinic acid in the cured specimen could be quantitatively analyzed by using HR/MAS NMR.

Under the condition of the consistent mass of specimens with 20 g succinic acid per 100 g UPR, ^1H HR/MAS NMR spectra was obtained and shown in Figure 10 at different pre-esterification time. Meanwhile, experimental ^1H HR/MAS NMR chemical shift, assignment and integral are listed in Table II.

This table is used to demonstrate the chemical shift, assignment and integral of ^1H HR/MAS NMR spectra.

The methylene of succinic acid did not take part in the pre-esterification, and the proton integral area of the group was set as 1.000. The proton integral area of the carboxyl group decreased from 0.037 for the succinic acid/UPR specimen at the pre-esterification time of 1.0 h to 0.016 when the pre-esterification time was 3.0 h. The quantitative changes in the HR/MAS NMR spectra apparently proved that the carboxyl group in succinic acid participated in the pre-esterification. With the prolongation of pre-esterification time, more carboxyl groups reacted with the excess dihydric alcohol hydroxyl groups to form esterifiable macromolecular compounds. This change was also reconfirmed by FTIR qualitative analysis.

Scanning Electron Microscopy (SEM) Experiment

The SEM micrographs of the UPR, the UPR with PVAc and the UPR with succinic acid in addition of 20 g per 100 g UPR are shown in Figure 11.

Figure 11(a) illustrates that due to the rapid cross-polymerization of UPR and the homopolymerization of polyesters, the internal stress had not been released thoroughly, resulting in cracks and micro voids obviously in the cured UPR specimen. Besides cracks and micro voids, phase separation also emerges in the specimen of PVAc/UPR as shown in Figure 11(b). The flexural strength of the PVAc/UPR specimen is decreased for the cracks, micro voids and phase separation. As for the succinic acid/UPR specimens, the low exotherm and slow polymerization rate of UPR caused by succinic acid made the internal stress release and the cracks decrease obviously. Therefore, a homogeneous morphology without cracks and micro voids is observed in Figure 11(c–e), corresponding to the pre-esterification time of 1.0, 2.0, and 3.0 h, respectively. That is the reason why the succinic acid/UPR specimen presented excellent antishrinkage and flexural strength.

CONCLUSIONS

Succinic acid was applied as a small molecule LSA in the anti-shrinkage of UPR in this study. The volume shrinkage of the cured UPR was $0.41 \pm 0.02\%$ and the flexural strength was 54.33 ± 1.90 MPa corresponding to the content of 20 g succinic acid per 100 g UPR at the pre-esterification time of 3.0 h. These properties of the cured UPR were significantly improved with

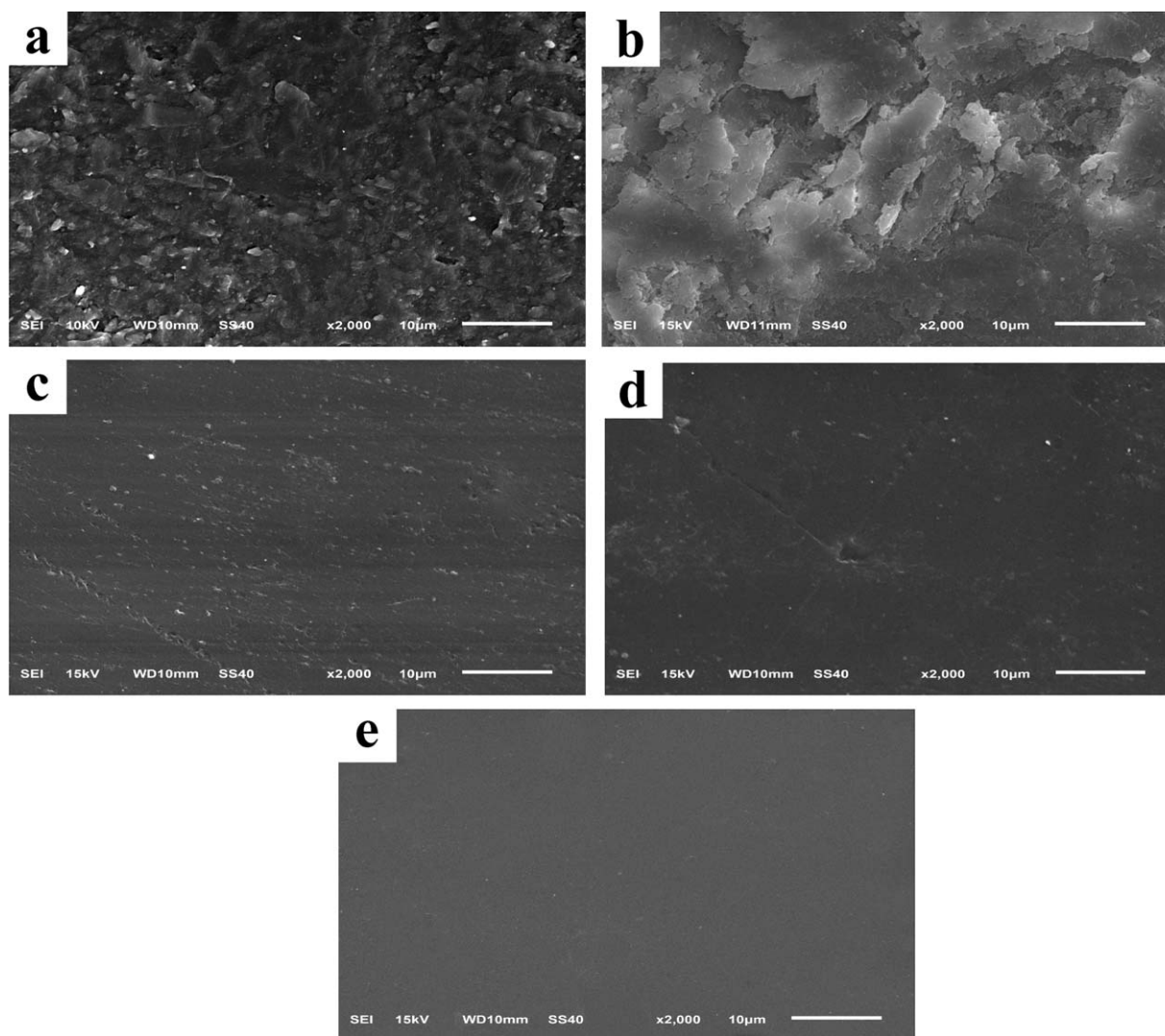


Figure 11. The SEM micrographs ($\times 2K$) of (a) the cured UPR, (b) the UPR with PVAc, (c–e) the UPR with 20 g succinic acid per 100 g UPR at pre-esterification time of 1.0, 2.0, and 3.0 h.

the presence of succinic acid. These advantages of succinic acid made it a candidate for industrial application.

Through the analysis of FTIR, DSC, HR/MAS NMR, and SEM, the antishrinkage mechanism of succinic acid was attributed to the pre-esterification with the formation of aqua and thermoplastic polyester. With the presence of aqua, the polymerization rate was slowed down and a revolution of polymerization of UPR was realized. The previous two-stage curing process, i.e., the cross-polymerization of UPR and the homopolymerization of polyester, changed to a one-stage curing process of UPR with styrene. Besides the decrease of structural shrinkage caused by aqua, thermoplastic polyester resulted in lower polymerization exotherm, leading to a decrease of thermal shrinkage. The internal stress released in the lower exotherm process, and the homogeneous micro-structure formed without cracks and micro voids. As a result, an optimal polymerization of the UPR was realized and the cured UPR exhibited low volume shrinkage. It

was evident that succinic acid, as compared with macromolecule LSAs and 2,2-dimethyl malonic acid, performed better effects on the polymerization of the UPR, as well as the micro-structure of the cured UPR.

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