Self-Cross-Linking Characterization of Poly(fumaric-*co*-itaconic-*co*-butanediol)

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The poly(fumaric-*co*-itaconic-*co*-butanediol) [poly(FA-*co*-IA-*co*-BD)] was prepared with fumaric acid (FA), itaconic acid (IA) and 1,4-butanediol (BD) by melt polycondensation. The insoluble gel fraction (Q_s), as the cross-linking degree of cured poly(FA-*co*-IA-*co*-BD) which could be self-cross-linked at high temperature through C=C in it, was got by Soxhlet extraction. The properties were investigated by FT-IR, ^{1}H NMR, DSC and XRD. The results indicated that Q_s increased with itaconic acid under the same treating condition. When the mole ratio of fumaric acid and itaconic acid approached to 1, the polyester had the highest Q_s (78.13 %) and the maximum rate constant k (0.2552 s^{-1}) after being treated at 150 ℃ for 20 min. As Q_s increased from 0 to 89.01 %, T_m decreased from 77.5 to 60.1 ℃, ΔH_m and the crystallinity decreased from 36.48 to 23.98 J g^{-1}, 43.10 to 26.30 %, respectively. And the biodegradation of the cross-linked polyesters became worse.

Key Words: Fumaric acid, Itaconic acid, Gel-fraction, Rate constant, Self-cross-linking.

INTRODUCTION

Unsaturated aliphatic polyesters condensed with unsaturated acid, *e.g.* maleic acid or fumaric acid, a dihydric alcohol were used in our daily life[1,2] and researched on their synthesis and physicochemical properties over past few decades[3,4]. The additive property of C=C in the unsaturated aliphatic polyesters has received considerable attention, because it would expand the possible application, for example, biomedical area, agricultural area, biodegradable plastics, toner and polyurethane[5,6].

The addition reaction of the C=C in unsaturated polyesters with a vinyl monomer as the cross-linking agent in the presence of a peroxide catalyst has been investigated. It was known that the linear polyesters chain could be cross-linked to network under certain conditions and then the properties of the polyesters were changed[7-12].

Aoyagi *et al.*[13-15] prepared cross-linked poly(ε-caprolactone-*co*-D,L-lactide) materials derived from 4-armed corresponding macromonomer and found that the drug permeation could be controlled by temperature change. The softening point and the mechanical properties of the cross-linked polyesters could be achieved by suitable mixing of the 2-branched poly(ε-caprolactone-*co*-D,L-lactide) macromonomer and the 4-branched ones.

It is showed that the degradation rate of the cured polymer was reduced with an increased degree of cross-linking. The biodegradability of PBS was remarkably reduced after chain extension with benzoyl peroxide. Tawfik *et al.*[16] found

that the C=C of maleic acid and fumaric acid present in the backbone was more susceptible to cross-link with styrene than the C=C of itaconic acid and the properties of the polyesters such as chemical resistance, flammability, thermal stability, physical, electrical and weathering properties could be affected by the type of glycol and the unsaturated acid. Shaeifi *et al.*[17] found that the mechanical properties of poly(ε-caprolactone-co-D,L-lactide) could be improved by cross-linking reaction.

The properties of cross-linked polyesters depended not only on the nature of individual components in the polyester chain, but also the type and ratio of the copolymerizable monomers that have participated in the cross-linking reaction. Much researches have been done on the effect of copolymerizable monomers on the properties of the cross-linked polyesters.

In the present study, we aimed to discuss the self-cross-linking characterization of poly(FA-*co*-IA-*co*-BD) synthesized from fumaric acid, itaconic acid and 1,4-butanediol (BD) by melt polycondensation. The C=C in fumaric acid is present in the backbone, while the C=C in itaconic acid is in the side chain. The effect of self-cross-linking temperature, self-cross-linking time and the monomer on Q_s (the per cent of insoluble gel fraction) were discussed and characteristics such as, T_m, ΔH_m, the crystallinity and biodegradation of the cross-linked polyesters were also discussed. Some parameters such as Q_s, self-cross-linking reactive ratio, the rate constants of self-cross-linking were also discussed.

EXPERIMENTAL

Fumaric acid (FA, CP), itaconic acid (IA, CP), 1,4-butanediol (BD, CP) and tin(II) chloride dihydrate (SnCl$_2$, AR) are purchased from Sinopharm Chemical Regent Co. Ltd. and they are reagent grade products. Lipoplase 100 L TYPE EX (LAP40018) is are purchased from Nonvzymes.

Fourier transform infrared (FT-IR) spectra were recorded on NEXUS-670 Fourier transform infrared spectrometer (Thermo Nicolet, USA). The 600 MHz ^{1}H NMR spectra were measured on a Bruker ARX spectrometer with samples dissolved in deuterated chloroform(CDCl$_3$) containing 0.03 or 1.0 vol % tetramethylsilane as the internal reference. The intrinsic viscosity [η] was measured by one-point method with of 0.75 % w/v polymer solutions in chloroform at 35 °C in a constant-temperature bath using an Ubbelohde viscometer. Melting temperature (T$_m$) and melting enthalpy (ΔH$_m$) were measured by differential scanning calorimetry (DSC) on a NETZSCH DSC 204F1 apparatus (NETZSCH instruments, Germany). The samples were scanned from 25 °C to 200 °C at a heating rate of 10 °C/min under nitrogen stream. The X-ray diffraction (XRD) patterns were obtained by using a D/max-2500 PC diffractometer with CuK$_a$ radiation, the data were collected in the 2θ ranged from 5 to 60°. Chloroform is a good solvent for the polyesters but not for the self-cross-linked polyesters. After being treated at high temperature, Soxhlet extraction was used to get the insoluble gel fraction (Q$_s$). The biodegradation of polyesters were carried out with lipase in standard phosphate buffer solutions (pH = 7.4, 37 °C) and the weight remaining of the polyester was used to describe the degree of biodegradation[18].

Synthesis of poly(FA-*co*-IA-*co*-BD): The polyconden-sation was conducted in bulk with stirring in an oil bath using the following optimum conditions. The mole ratio of diacid to diols was 1:1.1 and the mole ratio of fumaric acid and itaconic acid was from 1:0 to 0:1. The diacid and diols were placed in a round-bottom flask and 0.3 % (mole/monomer) was added under nitrogen flow. The round-bottom flask was immersed in an oil bath for *ca.* 5 h at 140 °C until over 70 % of the theoretical amount of by-product (water) was completely distilled out. Subsequently, the reaction mixture was gradually evacuated to *ca.* 20 mm Hg and heated to 180 °C for another 5 h. After cooling, the resultant crude product was dissolved in chloroform and poured into methanol for re-precipitating the polyester. The precipitate was washed with methanol twice and with diethyl ether and dried *in vacuo* for 3 days at ambient temperature[18].

Preparation of self-cross-linked samples: Each of the polymer samples was dissolved in chloroform in a concen-tration of 5 g dL^{-1} and cast into a Petri dish which had primarily been surface-treated with Sigmacoat (Aldrich) to prevent adhesion of the cast film. After solidification by air-drying, the film obtained was obtained after drying in vacuum at 60 °C or 80 °C for 4.0 h. Then the film was treated in an oven for 5~30 min at high temperatures (120~190 °C) in air.

RESULTS AND DISCUSSION

Composition and structure of poly(FA-*co*-IA-*co*-BD)[19]: The chemical structures of poly(FA-*co*-IA-*co*-BD) were confirmed by ^{1}H NMR. ^{1}H NMR (CDCl$_3$): δ = 6.86 (CO**CH**= **CH**CO), δ = 6.33~6.53, 5.67~5.92 (COC(=**CH**$_2$)CH$_2$CO), δ = 4.12~4.25 (COO**CH**$_2$CH$_2$CH$_2$**CH**$_2$OH), δ = 1.63~1.80 (COOCH$_2$**CH**$_2$**CH**$_2$CH$_2$OH), δ = 3.34 (COC(=CH$_2$)**CH**$_2$CO). According to integral area ratio of ^{1}H NMR signals of CO**CH**= **CH**CO and COC(=**CH**$_2$)CH$_2$CO, it could calculate the mole ratio of fumaric acid and itaconic acid. For example, the poly(FA-*co*-IA-*co*-BD) of the theoretical mole ratio of fumaric acid and itaconic acid = 1:1 and the actual mole ratio of fumaric acid and itaconic acid = 1:0.96 was calculated from the ^{1}H NMR which was shown in Fig. 1. The mole ratio of the fumaric acid and itaconic acid in the following section was the actual mole ratio calculated from the ^{1}H NMR.
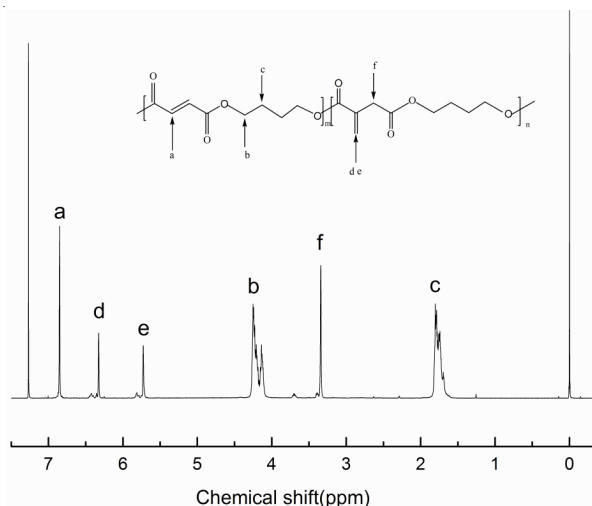

Fig. 1. ^{1}H NMR of poly(FA-*co*-IA-*co*-BD)
Note: The mole ratio of FA and IA in poly(FA-*co*-IA-*co*-BD) was 1:0.96

Fig. 2 showed the FT-IR spectra of poly(IA-*co*-BD) (a), poly(FA-*co*-IA-*co*-BD) (b, the mole ratio of fumaric acid and itaconic acid was 1:0.96) and poly(FA-*co*-BD) (c), respectively. There was a broad absorption peak around 1650 cm^{-1} in spectrum of a, b, c, which was the characteristic absorption peak of the C=C group. And broad absorption band around 1735 cm^{-1} attributed to the C=O group, asymmetrical C(=O)-O-C stretching band at 1140 cm^{-1} were evident and could be found. The broad absorption band around 2940 cm^{-1} attributed to C-H. It confir-med the formation polyesters was expected.
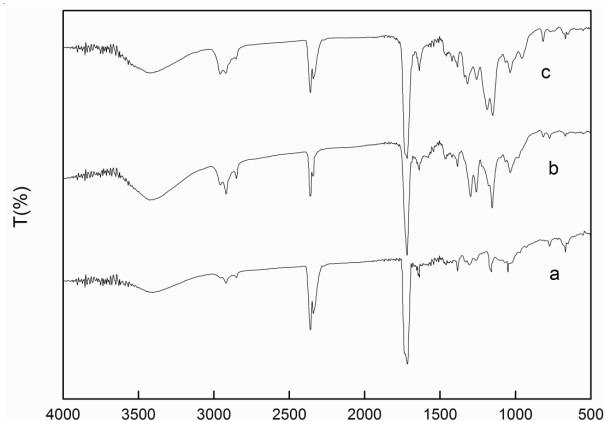

Fig. 2. FITR of poly(FA-*co*-IA-*co*-BD)
Note: a, b, c represented poly(IA-*co*-BD), poly(FA-*co*-IA-*co*-BD) (the mole ratio of FA and IA was 1:0.96) and poly(FA-*co*-BD), respectively

Self-cross-linking of the poly(FA-*co*-IA-*co*-BD): Unsaturated aliphatic polyesters could be cross-linked through their C=C *via* the appropriate vinyl monomers, usually styrene, in the presence of a peroxide catalyst. These polyesters are not self-cross-linkable unless being treated either at high temperature or over lengthy times. As the introduction of C=C into backbone of polyesters, the linear chain could be changed to reticular formation under certain condition. In present study, all samples were heat-treated for different time at different temperatures without cross-linking agent and self-cross-linked by C=C in unsaturated aliphatic polyester to form network. Soxhlet extraction was used to get the insoluble gel fraction (Q_s). For example, the results of poly(FA-*co*-IA-*co*-BD) (the mole ratio of fumaric acid and itaconic acid = 1:0.96) were shown in Figs. 3 and 4.
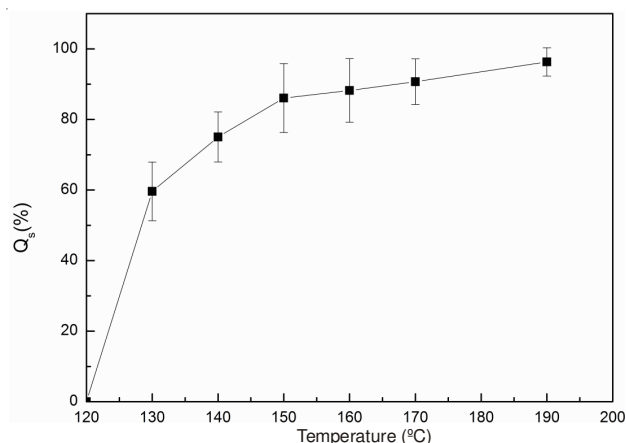

Fig. 3. Effect of self-cross-linking temperature on Q_s when self-cross-linking time was 25 min
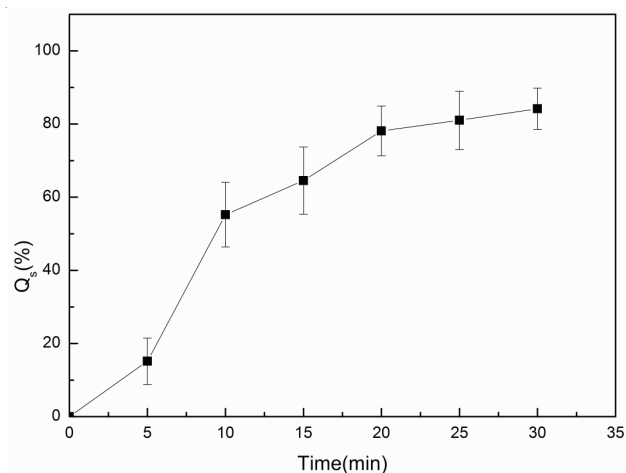

Fig. 4. Effect of self-cross-linking time on Q_s when self-cross-linking temperature was 150 ºC

Fig. 3 depicted the Q_s of the polyester self-cross-linked at different temperatures for 25 min. It could be seen from Fig. 3 that with the increase of the temperature from 120 to 190 ºC, the Q_s of the polyester increased. After the self-cross-linking temperature above 150 ºC, the Q_s did not change obviously. Fig. 4 showed the effect of the self-cross-linking time on Q_s at 150 ºC. It could be seen that Q_s reached the equilibrium value (78 %) when the self-cross-linking time was 20 min. So the optimum treatment condition was 20 min and 150 ºC.

Except the self-cross-linking temperature and self-cross-linking time, the factors affected the Q_s of the copolymers also include the materials itself[20,21]. All samples were treated at 150 ºC for 20 min and Fig. 5 showed the effect of different compositions on Q_s of poly(FA-*co*-IA-*co*-BD). The characteristics of these copolymers were shown in Table-1. It could be seen from Fig. 5 that when the mole ratio of fumaric acid and itaconic acid approached 1 (1:0.96), a maximum value of Q_s in the poly(FA-*co*-IA-*co*-BD) was found.
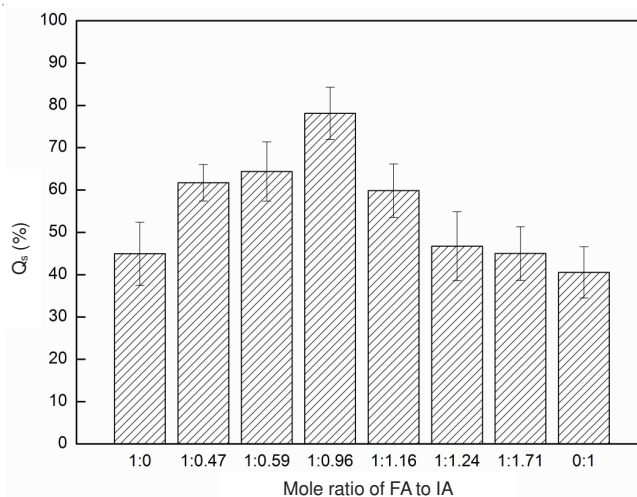

Fig. 5. Effect of different compositions of poly(FA-*co*-IA-*co*-BD) on Q_s

TABLE-1 CHARACTERISTICS OF POLY(FA-co-IA-co-BD)				
Actual n(FA):n(IA)	[η] (mL g^{-1})	Appearance	T_m (ºC)	Crystallinity (%)
1:0	18.88	White solid	142.1	65.80
1:0.47	17.93	White solid	100.1	49.18
1:0.59	17.78	White solid	87.4	48.23
1:0.96	17.47	White solid	77.5	43.10
1:1.16	17.19	White solid	65.7	28.69
1: 1.24	17.01	White solid	46.0	23.73
1:1.71	16.14	Light yellow cream	-	-
0:1	15.59	Yellow viscous liquid	-	-

Note: n (FA): n (IA) represented the mole ratio of FA and IA, the ratio of diacid and diols was 1:1.1

Self-cross-linking kinetics of poly(FA-*co*-IA-*co*-BD): The insoluble gel fraction (Q_s) of self-cross-linked polyesters was obtained from the cross-linking degree. $1-Q_s$ indicated the content of residual C=C and it was proportional to the concentration of the monomer C=C. Through plotting, $1/(1-Q_s)$ and self-cross-linking time had a linear relation, the correlation coefficient was about 0.99, which was shown in Fig. 6. The self-cross-linking reaction was supposed to a pseudo-second-order reaction and the slope of the line was equivalent to the rate constant of the self-cross-linking reaction. The results of self-cross-linking reaction at 150 ºC were shown in Table-2.

It could be seen from Table-2 that the rate constant k of the poly(FA-*co*-IA-*co*-BD) (the mole ratio of fumaric acid and itaconic acid = 1:0.96) was bigger than other rate constants. This implied that the C=C in the poly(FA-*co*-IA-*co*-BD) (the mole ratio of fumaric acid and itaconic acid = 1:0.96) reacted faster than in other polyesters, so in the same self-cross-link

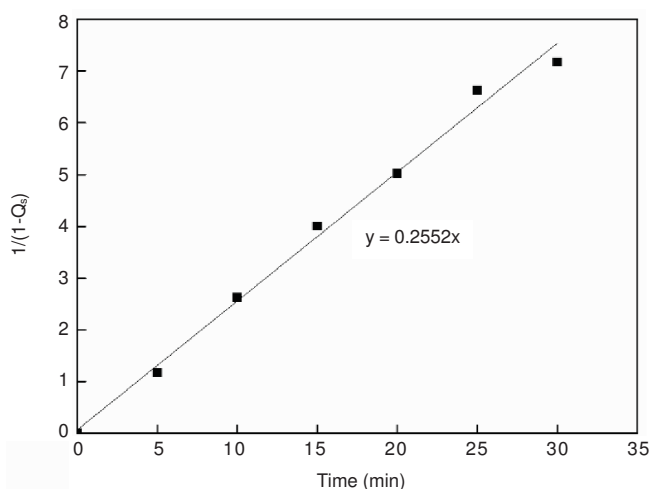| TABLE-2 RATE CONSTANTS OF POLY(FA-co-IA-co-BD)								
Sample	1:0	1:0.47	1:0.59	1:0.96	1:1.16	1:1.24	1:1.71	0:1
Rate constant(s^{-1})	0.0375	0.0612	0.0635	0.2552	0.0922	0.0823	0.0819	0.0701

Fig. 6. Plot of 1/(1-Q$_s$) *vs.* time (t)

ing time and temperature, the poly(FA-*co*-IA-*co*-BD) (the mole ratio of fumaric acid and itaconic acid = 1:0.96) had the highest Q$_s$, which coincide with the results of Fig. 5.

To calculate the polymerization rate or polymer productivity and composition, monomer reactivity ratio must be known[22,23]. Reactivity ratios were among the most important parameters for the composition equation of copolymers, which could offer information such as the reactivity of monomers pairs and help estimate the copolymer composition. The reactivity ratio of fumaric acid and itaconic acid were calculated through the Kellen-Tudos method as follows:

$$r_F = \frac{Q_F}{Q_I}\exp[-e_F(e_F - e_I)] \qquad (3)$$

$$r_I = \frac{Q_I}{Q_F}\exp[-e_I(e_I - e_F)] \qquad (4)$$

The Q$_F$ and e$_F$ parameters calculated in this work for fumaric acid are equal to 0.51 and 0.94, respectively[24]. And Q$_I$ and e$_I$ for itaconic acid are 0.5 and 0.76, respectively. Through Formula 3 and 4, r$_F$ = 0.496, r$_I$ = 1.66. The r$_F$ × r$_I$ = 0.823 (<1) of the product indicated that during the reaction of C=C in itaconic acid and fumaric acid, their capability of copolymerization was greater than the homopolymerization. So, the poly(FA-*co*-IA-*co*-BD) (the mole ratio of fumaric acid and itaconic acid = 1:0.96) had the highest Q$_s$.

Effect of self-cross-linking on properties of poly(FA-*co*-IA-*co*-BD): The properties of polymer depended mainly on the structure and unsaturated aliphatic polyesters were no exception. The C=C could self-cross-link at high temperature for a long time and then the properties of the polyester were changed after being heat-treated.

Due to the excellent self-cross-linking characteristic of poly(FA-*co*-IA-*co*-BD) (the mole ratio of fumaric acid and IA = 1:0.96), the properties with different Q$_s$ were shown in Table-3.

From Table-3, it could be seen that T$_m$, ΔH$_m$ and the crystallinity decreased with the increase of Q$_s$ and the biodegradation of self-cross-linked poly(FA-*co*-IA-*co*-BD) became worse in lipase. The results were in accord with common view of crystalline polymer cured. When the melt cooled down, the existance of self-cross-linking point would hinder the movement and arrangement of molecular chain, then the regularity of crystalline region decreased. After being self-cross-linked at high temperature for a long time, the linear macromolecules were changed into netted structures. Then the enzyme was not permeated easily into the polyesters and the biodegradation of the self-cross-linked poly(FA-*co*-IA-*co*-BD) became worse.

TABLE-3 EFFECT OF SELF-CROSS-LINKING ON PROPERTIES OF POLY(FA-co-IA-co-BD) [n(FA):n(IA) = 1 : 0.96]				
Q$_s$ (%)	T$_m$ (ºC)	ΔH$_m$ (J g^{-1})	Crystallinity (%)	Weight remaining* (%)
0	77.5	36.48	43.10	89.68
15.73	72.5	34.19	39.32	92.22
22.85	72.2	34.45	32.34	92.74
40.58	70.9	34.22	29.57	95.02
56.71	66.6	28.69	29.33	95.66
71.17	63.5	26.08	28.34	96.23
81.01	61.8	24.76	27.61	98.31
89.01	60.1	23.98	26.30	98.56

*Represented the weight remaining of self-cross-linked polyesters after 7 day's enzymatic degradation

Conclusions

In this paper, we studied the self-cross-linking characteristics of poly(FA-*co*-IA-*co*-BD) which was synthesized from fumaric acid, itaconic acid and BD by melt polycondensation. The results are:

(1) The Q$_s$ increases with the self-cross-linking temperature and time and the present unsaturated aliphatic copolymers have excellent self-cross-linking characteristics at high temperature.

(2) The self-cross-linking reaction was a pseudo-second-order reaction. When the mole ratio of fumaric acid and itaconic acid was 1:0.96, poly(FA-*co*-IA-*co*-BD) had the highest rate constant (0.2552 s^{-1}) and Q$_s$ (74.3 %).

(3) With the increase of Q$_s$, the T$_m$ decreased from 77.5 ºC to 60.1 ºC, ΔH$_m$ decreased from 36.48 to 23.98 J g^{-1} and the crystallinity decreased from 43.10 to 26.30 %, respectively. The biodegradation of self-cross-linked polyesters became worse.

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