The Graft Copolymerization of Corn Starch by Microwave Irradiation with Rheological Phase Reaction

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ABSTRACT: The corn starch was grafted by microwave irradiation with rheological phase reaction, to meet the sizing requirements of polyester/cotton blended yarn and avoid the disadvantages of corn starch size including brittle, hard, and size shedding. On the basis of the damping characteristics of corn starch film and the polarity of grafting monomer, the grafting effect of grafted corn starch was researched by using infrared spectroscopy, SEM, rotary viscometer, and thermomechanical analyzer. The results showed that both hydrophilic groups and hydrophobic groups were introduced in the molecular chains of grafted corn starch. The storage modulus of grafted corn starch film reached 285–315 MPa, being four times higher than that of nongrafted corn starch film. Compared with corn starch sizing, the viscosity of grafted corn starch sizing decreased 62.5%. Furthermore, through analyzing grafting law and establishing regression equation, it was indicated that the irradiation time and initiator content influenced the grafting ratio of grafted starch significantly. The grafting ratio could reach 19.57%, when the irradiation time and initiator content were selected with 3.5 min and 4.55%, respectively. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1481–1487, 2011

Key words: Corn starch; graft copolymerization; microwave irradiation; rheological phase reaction

INTRODUCTION

Comparing with traditional methods, grafting starch by microwave irradiation with rheological phase reaction is a method of time-saving, high efficiency, low energy consumption, and less pollution.[1,2] The corn starch is easy to contact with monomer in rheological phase reaction system[3] because of its small size and large specific surface area. So the grafting ratio of corn starch is higher. Because the state of corn starch was granular, the products after grafing are separated conveniently, and disadvantages could be avoided, such as precipitation, high viscosity, high diffusion resistance of free radical, high content of homopolymer and unstable quality.[4,5]

The researches about grafted starch sizing focus mainly on how to improve grafting ratio. But the graft modification on corn starch used in sizing for special yarns seems to be very few. In this study, the molecular chain of grafted corn starch was designed to avoid the brittleness and hardness of the corn starch film. Thus grafted corn starch had better coating and permeability for polyester/cotton blending yarn and then the yarn hairiness and strength were improved. Furthermore, the suitable grafting monomers were chosen to improve the damping characteristics of corn starch film and increase the coating and permeability of corn starch sizing to the polyester/cotton blending yarns.

The requirements of grafting ratio for various linear density and blend ratio yarns are different. Therefore, the grafting law of grafted corn starch was investigated and the regression equation was established in this study with the aim at saving time and decreasing cost.

EXPERIMENTAL

Materials and equipment

Corn starch (ST), Purity 100% (Qishen Food Co.Ltd, Jilin province). Grafting monomer, Acrylic acid (AA) and Butyl methacrylate (BMA) (KRS Fine Chemical Co.Ltd, Tianjin), Dimethyl sulfoxide (DMSO), Analytical pure, Hydrochloric acid, Acetone, potassium persulfate (KPS) (KRS Fine Chemical Co.Ltd, Tianjin).

AA and BMA were refined by vacuum distillation and KPS was purified by recrystallization before using.

Galanz domestic microwave oven (WP800, 2450Hz, Guangdong Glanz company), Magnetic stirring heater (Yuhua Instrument Co.Ltd, Gongyi City), Balance (German Sartorius Company), SXT-06 Soxhlet extraction device (Shanghai Hongji Experimental Instrument Co. Ltd, Shanghai), Ubbelohde viscometer(Shanghai Dibai Experimental Instrument Co.

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Ltd, Shanghai), TENSON37-based Fourier transform infrared spectrometer (USA), Quanta200 scanning electron microscope (PEI's), NJ79 rotary viscometer (Jianyi Test Instrument company, Tianjin), PE1020 Series DSC7 differential scanning calorimeter (Perkin–Elmer Corp.), DMA242C thermal mechanical analyzer (Germany NETZSCH Company).

Grafting process

Totally, 15 g of corn starch was dispersed in 150 mL of deionized water, and the dispersion was stirred with 40 r/min for well-mixing and heated up to 60°C in a thermostatical tempreature waterbath for 30 min. Thus the pregelatinized corn starch with rheological phase was made.

About 3 mL of AA at 1.05 g/cm^3 and 7 mL of BMA at 0.895 g/cm^3 were added into the pregelatinized corn starch with stirring at 40 r/m, and then 12 μL of KPS and 0.6 g of DMSO were added into the starch with stirring as well. After that, the pregelatinized starch was put into a china-reacting-kettle and the kettle was put into a microwave oven in which the graft copolymerized reaction occurred. The irradiating manner was intermission, that is, after irradiating for 3.5 min, the kettle was taken out from the oven and the starch in it was stirred at 2.0 min, repeatedly irradiating four times and stirring three times. Then the grafted copolymers were obtained.

After they were immersed, cleaned, and filtrated by absolute ethyl alcohol, the grafted copolymers were dried with vacuum at less then 50°C. The primary grafted products were obtained. Then the grafted products were purified with absolute acetone solution for 8 h by a Soxhlet extraction device so as to remove homopolymers and then dried with vacuum at 50°C. Thus the grafted starch was made.

Totally, 2.00 g of the grafted starch was added into 100 mL of hydrochloric acid with 3 mol/L and hydrolyzed for 3 h at 80°C. I-KI solution was used to be ensure complete hydrolyzation. Then the grafted chain was obtained by purifying and drying with vacuum at 50°C. The grafting ratio can be calculated by eq. (1).

$$GR = \frac{\text{Grafted branch chain weight}}{\text{Grafted starch weight}} \times 100\% \quad (1)$$

Then the grafted starch was tested by infrared spectroscopy, SEM and DSC. The DSC's rate of heating is 10°C/min.

RESULTS AND DISCUSSION

Reaction mechanism

In microwave field, when the initiator-K2S2O8 is heated in aqueous medium, it decomposes to $SO_4^{-\bullet}$ and $^\bullet$OH free radicals. These generated free radicals attack the starch molecules chains and the starch free radicals are formed. Then they react with monomers-Acrylic acid (AA) and Butyl methacrylate (BMA) to initiate graft copolymerization. Subsequent addition of monomer molecules to the starch increases the size of the branched chain. When the two radicals react, the graft copolymerization is terminated.

M: monomers R: free radicals St: starch

Initiation:

$$R^\bullet + St{-}OH \rightarrow St{-}O^\bullet + RH$$
$$StO^\bullet + M \rightarrow St{-}OM^\bullet$$
$$R^\bullet + M \rightarrow M^\bullet$$

Propagation:

$$St{-}OM^\bullet + nM \rightarrow St{-}(M){-}M^\bullet$$
$$M^\bullet + nM \rightarrow (M)_n{-}M^\bullet$$

Termination:

$$St{-}O{-}(M)_n{-}M^\bullet + St - O{-}(M)_n{-}M^\bullet \rightarrow StO{-}(M)_n{-}MM{-}(M)_n{-}OSt$$

(graft copolymer)

$$St{-}O{-}(M)_n{-}M^\bullet + (M)_n{-}M^\bullet \rightarrow StO{-}(M)_n{-}MM{-}(M)_n$$

(graft copolymer)

$$(M)_n{-}M^\bullet + (M)_n{-}M^\bullet \rightarrow (M)_n{-}MM{-}(M)_n$$

(homopolymer)

Grafting effect

Infrared spectra

As Figure 1 shown, to investigate the grafting effect of the grafted starch by microwave irradiation with rheological phase reaction, both nongrafted starch and the grafted starch were tested by infrared spectroscopy. Figure 1 shows that the absorption peaks of the grafted starch appear at 3417 cm^{-1}, 2152 cm^{-1}, 1392 cm^{-1}, 1022 cm^{-1}, 548 cm^{-1}, which are also the characteristic absorption peak of corn starch. And also the absorption peak appears around 1730 cm^{-1}, which is the characteristic absorption peak of the ester and carbonyl group. This results indicates that the corn starch has been grafted and copolymerized with AA and BMA.

SEM

The morphology of nongrafted starch and grafted starch was studied by SEM, respectively. The results are shown in Figure 2. The oval particles with smooth surface and different size can be seen at the

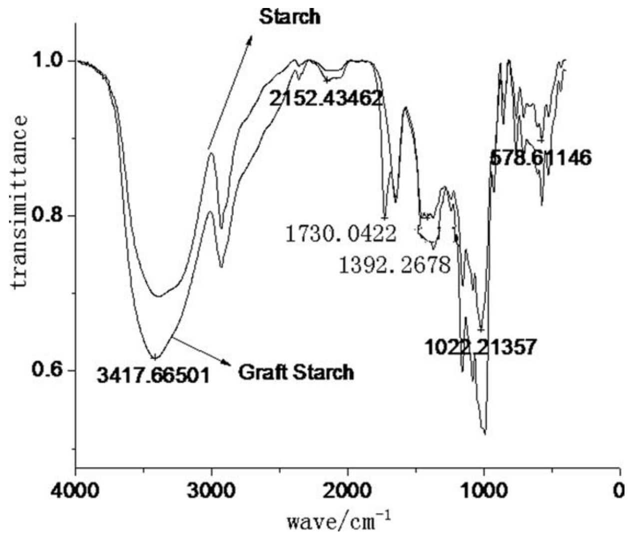

Figure 1 The infrared spectra of the nongrafted starch and grafted starch. A, nongrafted starch; B, grafted starch.

image of nongrafted starch as shown in Figure 2(a). However, the surface on the particles of the grafted starch as shown in Figure 2(b) is rough and some cracks are distributed on the surface as well. This results indicates that the monomers, AA and BMA, were be grafted onto the molecular chains of corn starch, that is, the graft copolymerization occurred between monomers and corn starch. And the morphological structure about grafted starch may be changed. Thus, the rheological property and viscosity of grafted starch sizes are improved greatly comparing with that of nongrafted corn starch sizes, as shown in Table I.

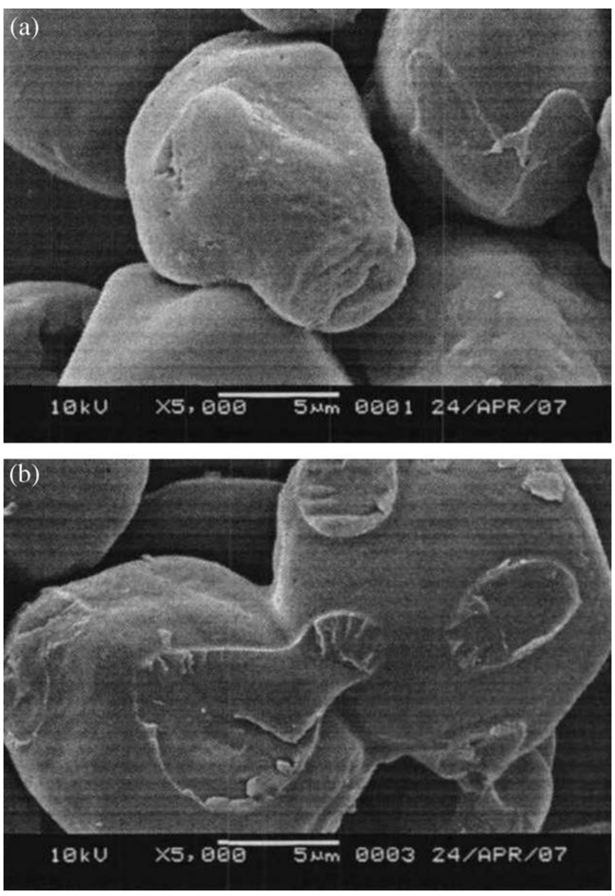

Figure 2 The SEM images of nongrafted starch and grafted starch (×4000). (a) nongrafted starch, (b) grafted starch.

TABLE I
The Viscosity of Grafted Starch Solution with Different Radiation Time

Radiation time (min)	0	2.0	2.5	3.0	3.5
Viscosity (mPa s)	82	52	50	40	30

Rheological properties

The grafted starch solution of 6% concentration was heated at 95°C for 3 h. And the viscosity was examined with different radiation time. The results are showed in Table I.

As can be seen, the viscosity of grafted starch solution is influenced by radiation time obviously. The longer the radiation time is, the lower viscosity the solution has. Because of the longer molecular chain and the higher molecular weight, the molecular chains in corn starch solution are difficult to move, so that solution has higher viscosity. With the radiation time increased, the number of short branched-chain introduced into corn starch molecular chain has increased. Therefore, the flexibility of molecular chain is increased. Moreover, the molecular is broken with resonating between the microwave irradiation and the starch. As a result, the molecular weight and the viscosity of grafted starch solution is reduced.

Dynamic mechanical behavior

Figure 3 displays the DSC curves of nongrafted starch and grafted starch. As can be seen, the glass transition region of nongrafted starch ranges from 267 to 290°C, while that of grafted starch ranges from 230 to 249°C. The T_g (glass transition temperature) of corn starch, grafted starch, BMA and AA are 278°C, 239°C, 30°C, and 87°C, respectively.[6]

According to Fox Design Principles, when polymers with different T_g occur copolymerization reaction, the T_g of copolymer locates in the both T_g of polymers. And the T_g value depends on the quantity of monomers.[7] After grafting, the T_g of grafted starch is higher than that of grafting monomer, but lower than that of corn starch, This result verifies that the grafted starch is produced by the graft copolymerization of corn starch, BMA and AA.

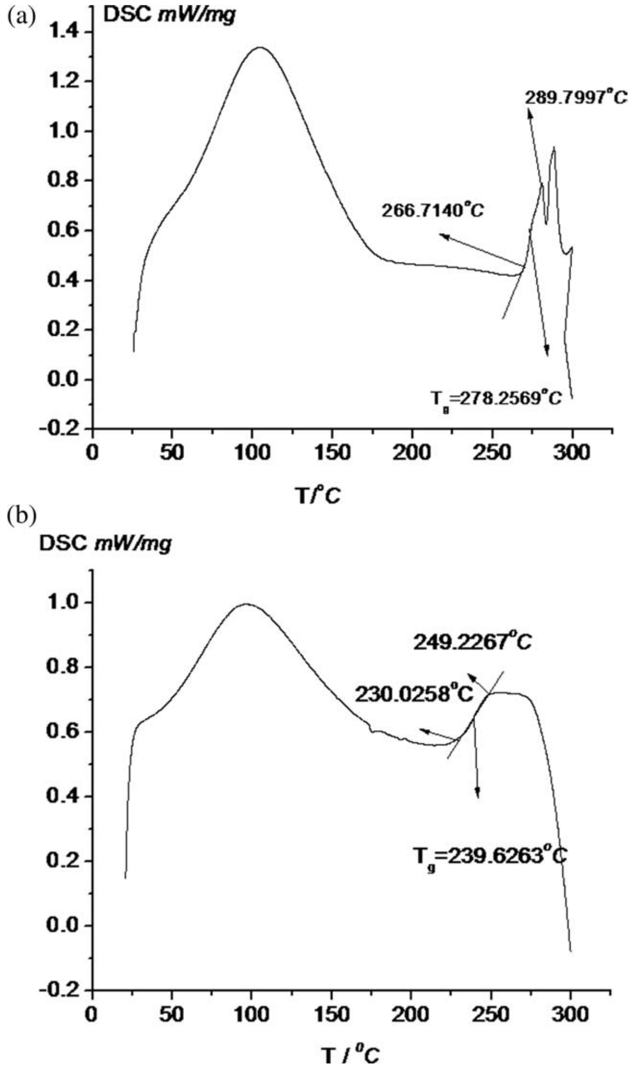

Figure 3 The DSC curves of nongrafted starch and grafted starch. (a) nongrafted starch, (b) grafted starch.

The DMA curves of nongrafted starch and grafted starch is shown in Figure 4. As shown, the storage modulus of grafted starch film (285 MPa–315 MPa) is higher than that of nongrafted starch (≤50 MPa). Compared with nongrafted starch film (9.8°C–74.3°C), the glass transition region of grafted starch film (7.0°C–47.4°C) has been broadened The storage modulus of grafted starch film is higher than that of nongrafted corn starch film because of the introduction of hard monomer into the corn starch molecular chains.[8] The hydroxyl in corn starch molecular chain is hydrophilic group while the ester group in BMA is hydrophobic group. The microscopic phase separation between those two different groups might be the reason for the broader glass transition region and the higher storage modulus in grafted starch film. Those above also verify that the grafting copolymerization happens among corn starch, BMA, and AA. According to the definition of complex modulus, the loss modulus of grafted starch film is higher than that of nongrafted starch film, because the film has higher storage modulus. Therefore, compared with nongrafted starch film, the damping characteristics of grafted starch film has been improved significantly, namely the energy dissipating ability is increased. Thus, in weaving process, the grafted starch sizing film could resist more mechanical forces. Therefore, the problems caused by corn starch in warp yarn sizing, such as hardness and brittleness, could be solved well.

The discussion of grafting law

The influence of the radiation time on grafting ratio

As shown in Figure 5, the grafting ratio increases firstly and then decreases with the radiation time increasing. The maximum grafting ratio of 19.20% will be reached after radiating for 3.5 min. The gelatinization of corn starch solution was influenced by radiation time obviously during the graft copolymerization of corn starch by microwave irradiation with rheological phase reaction.

The effect of radiation time on the gelatinization of starch solution is shown in Figure 6. The corn

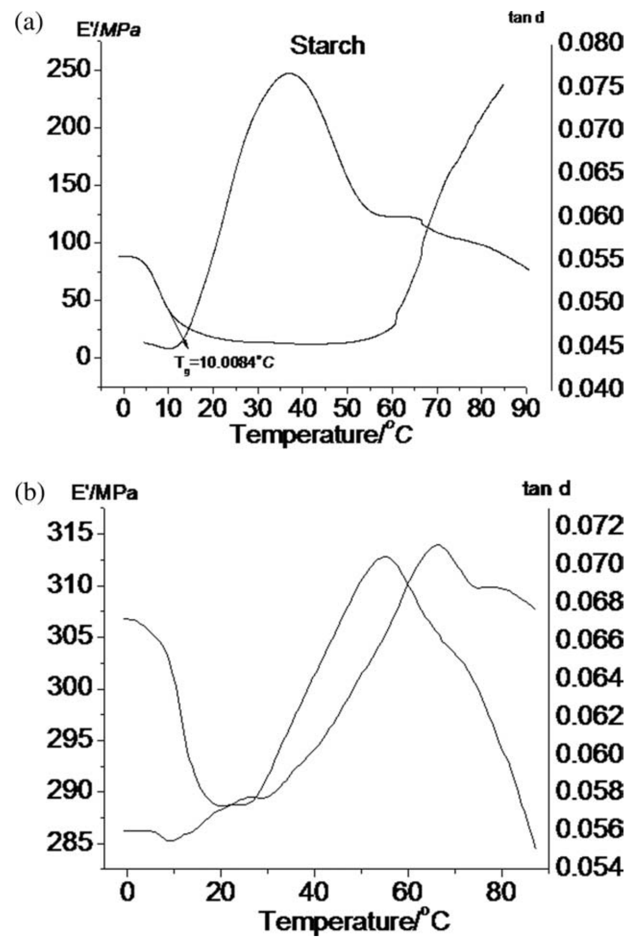

Figure 4 The DMA curves of nongrafted starch and grafted starch. (a) nongrafted starch, (b) grafted starch.

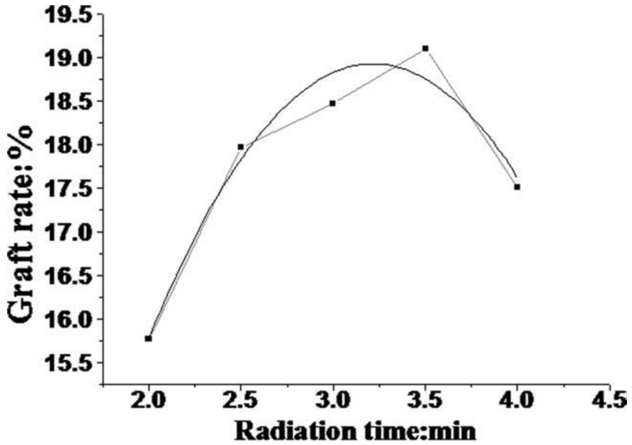

Figure 5 The influence of radiation time to grafting ratio. The smooth curve is fitting curve of grafting ratio and radiation time. The other is the broken line which connects the test data

starch solution expressed a low gelatinization degree due to the short radiation time and low thermal effect. Since corn starch particles have large size and small specific surface area,[9] the small gap among corn starch particles makes the accessibility between corn starch particles and grafting monomers difficulty so that the grafting ratio of grafted starch is lower. Additionally, the chemical energy of grafting reaction is decreased for renonant between microwave and the chemical bond of starch molecular chains. In case of short radiation time, the activity of starch molecular chains cannot be excited, which leads to a low graft reacting efficiency and grafting ratio. As increasing radiation time, the gelatinization degree of starch is enhanced greatly due to a high microwave themol effect. Thus the corn starch particles become smaller and the specific surface area becomes larger. In this case, corn starch particles can contact with grafting monomers uniformly. And the movement ability of corn starch molecular chain is high enough. As a result, corn starch obtains high grafting ratio. However, exceeded radiation time (4 min) will leads to a marked increase on the viscosity of starch solution which would be harmful for sizing.

TABLE II
The Influence of Radiation Time on the Viscosity of Starch Reaction System

Radiation time (min)	0	2.0	2.5	3.0	3.5	4.0
Viscosity (mPa s)	4.5	5.0	5.0	9.0	13.0	45.0

Table II indicates the effect of radiation time on the viscosity of corn starch solution. The longer the radiation time is, the higher viscosity the solution has. After radiating 3.5 min, the viscosity of solution increases sharply with the radiation time increasing, reaching 45.0 mPa S at 4.0 min. The diffusion resistance of free radical is increased sharply and the grafting ratio would be low as well at exceeded radiation time. So, the grafting ratio reaches the maximum at 3.5-min radiation time.

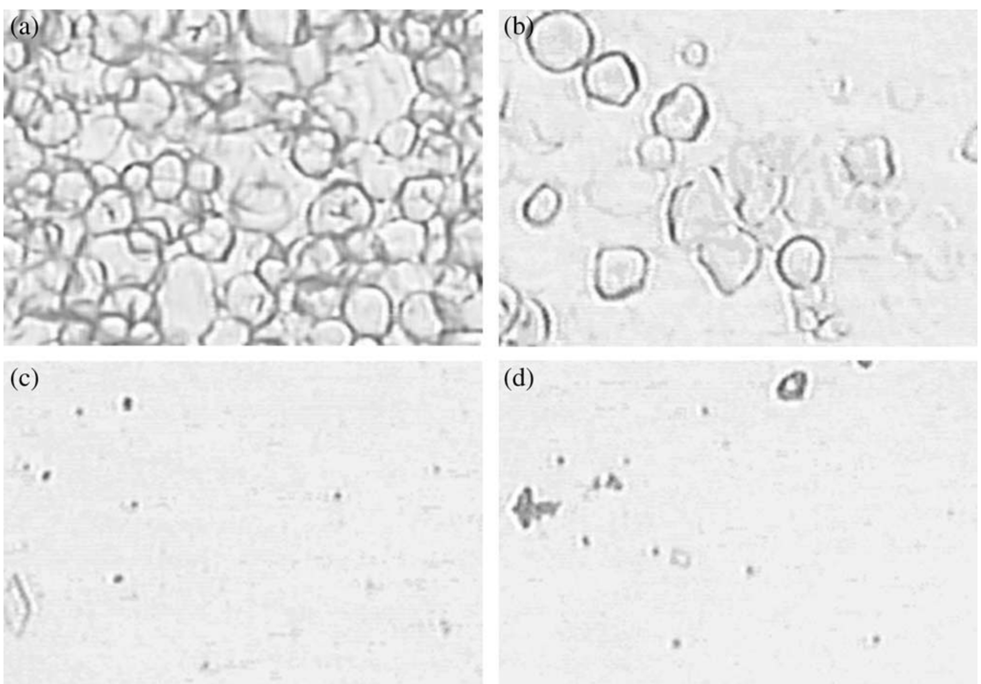

Figure 6 The influence of radiation time on the degree of starch gelatinization (×100). (a) 2.5 min, (b) 3.0 min, (c) 3.5 min, (d) 4.0 min.

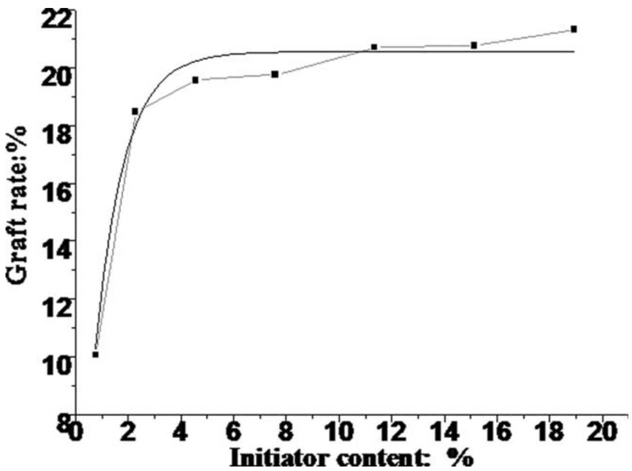

Figure 7 The influence of initiator content on grafting ratio. The smooth curve is the fitting curve of grafting ratio and initiator content. The other is the broken line which connects the test data.

The influence of initiator content on grafting ratio

Figure 7 shows the influence of initiator content on grafting ratio at 3.5 min radiation time. The grafting ratio increases first, and then becomes constant with the initiator content increasing. During the grafting, SO_4^{-2} and OH^- are released as KPS reacting with H_2O, which could initiate for the corn starch to produce St •. The free radical of St reacts with grafting monomer. And then, the grafted starch is produced. The Rheological phase reaction is beneficial to grafting corn starch due to much H_2O existing in the reacting system. Moreover, the high solubility of KPS in H_2O makes the phase separation between solid and liquid unobvious and then the diffusing resistance of free radical decreasing. This is beneficial to grafting. As the initiator content increases, the increasing concentration of free radical makes the grafting ratio higher. However, when the concentration of free radical increases to a certain value, the grafting rate is a constant. In this case, the probability of contacting among primary free radicals and forming homopolymer may become stronger. All above make the homopolymer content increase instead of grafting ratio. When initiator content is more than 4.55 wt %. The content of homopolymer increases sharply with initiator content increasing. On the basis of the quality and cost, when radiation time and initiator content are 3.5 min and 4.55%, respectively, the grafting ratio reaches 19.57%, which could be the optimized parameters for grafting corn starch by microwave reaction with rheological phase.

The correlation between grafting ratio and the reaction conditions

In fact, different linear density and blending ratio of yarns may demand grafted starch having different grafting ratio. So, more time and high cost could be needed to aim the goal.[10,11] In this study, the regression equation of grafting law is established by Origin7.0 software, by which the grafting ratio meeting different demand would be predicted efficiently. The smooth curves in Figures 5 and 7 are fitting curves of grafting ratio and radiation time, initiator content separately. The regression equations of two fitting curves are showed as eqs. (2) and (3),

$$y_1 = -3.9827x_1^2 + 14.28886x_1 - 2.21714 \quad (2)$$

$$y_2 = 20.5552 \times (1 - 0.4009^{x_2}) \quad (3)$$

where y_1, y_2 is grafting ratio, x_1 the radiation time, x_2 the initiator content.

The correlation coefficient between grafting rate and irradiation time is 0.95629, as the initiator content 0.97812. So the correlations of grafting ratio and irradiation time and initiator content are significant. Therefore, the equations would be used for predicting the grafting ratio of the grafted starch in the microwave field.

CONCLUSION

The corn starch was grafted with properly selected monomers by microwave irradiation with rheological phase reaction. The molecular chains of corn starch were introduced to hydrophilic groups and hydrophobic groups so as to be suitable for hydrophilic/hydrophobic fiber blending yarn.

The damping characteristics of corn starch film were improved greatly after grafted modification. Compared with corn starch film (≤50 MPa), the storage modulus of grafted starch film (285–315 MPa) was greatly improved. The glassy transition temperature region of grafted starch film (9.8°C–74.3°C) was wider than that of corn starch (7.0°C–47.4°C), which made the damping characteristics of grafted starch film keep good durability in a wider temperature range. The effect of the radiation time on the viscosity of the grafted starch sizing was significant. The longer the radiation time was, the lower the viscosity of grafted starch sizing would be. When the radiation time reached 3.5 min, the viscosity of grafted starch sizing was decreased from 82 mPa·s of the corn starch to 30 mPa·s, and reduced by 62.5%. It was obviously that the radiation time and initiator content influenced grafting ratio. The grafting ratio increased first, and then decreased with the radiation time increased. The grafting ratio increased first, and then kept unchangeable with the increase of initiator content. On the basis of the quality and cost, the optimal grafting process was radiation time of 3.5 min, initiator content of 4.55%, at which the grafting ratio reached 19.57%.

Starch was widely used in warp sizing for its easily degradable and environment-friendly characters.

However, it is mainly used for natural hydrophilic yarns. Despite of the advantages of starch, the grafted starch can own different properties due to the introduction of different grafting monomers, expanding the scope of application. For example, introducing hydrophobic groups into starch can make it used in hydrophobic yarns, this kind of grafted starch can replace PVA partly even all as sizing materials. Through the analysis of the relationship between microwave radiation time, initiator content, and the grafting rate, we can use resources more reasonable and it will be helpful in industrial production.

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