Synthesis and Properties of Starch-Grafted Polystyrene-Maleic Anhydride Copolymer

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ABSTRACT: The typical process used to synthesize expandable polystyrene was modified and applied to prepare water expandable polystyrene (WEPS)-starch copolymer. The maleic anhydride was used to improve the compatibility between starch and styrene. Various reaction conditions, weight ratio of styrene/water (O/W ratio), and starch content, were applied to obtain WEPS copolymer beads. Molecular weight, molecular weight distribution, glass transition temperature (T_g), and phase behavior of copolymer were investigated. With the increase of O/W ratio, the water content and molecular weight increased, whereas the molecular weight distribution and T_g of copolymer decreased. Molecular weight distribution and the T_g of the copolymer both increased as a function of starch content. The water content in the beads reached the maximum value at 6 wt % of starch content at same O/W ratio. The domain size of starch increased with the increase of the starch content. The domain size distribution of starch was best at 6 wt % of starch. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: expandable polystyrene; water; starch

INTRODUCTION

Expandable polystyrene (EPS) has lots of virtues, such as light weight, low cost, low thermal conductivity, good electricity, sound insulation etc., especially as a kind of moisture-proof and aseismatic material. Because of simple and convenient molding technique, it is often used as package material of electrical appliance, instrument, glass products and electrical products, even for food industry. Conventional EPS is prepared via the suspension polymerization of styrene containing volatile organic compounds (VOCs), such as pentane isomers, as the physical blowing agents. The blowing agents are introduced into the closed suspension reaction vessel during the final stage of polymerization.[1–3] When the beads are processed, the temperature must be higher than the T_g of PS for pre-expansion. The higher T_g of the matrix, the less residue of the blowing agent. Therefore, a lot of work[4–6] has been done

for raising the T_g of EPS through copolymerization with different monomers, such as α-Methylstyrene.

All of organic blowing agents, such as pentanes, are harmful to human health and the environment.[7,8] VOCs contribute to the generation of ozone in the lower atmosphere. Extensive studies have shown that ozone is both a lung irritant and a phytotoxin. It is responsible for crop damage and is suspected of being a contributor to forest decline in Europe and the United States. Besides, VOCs such as pentane are precursors for a multitude of other photochemical smog species that also have significant environmental consequences. Moreover, carbon dioxide, which contributes to the greenhouse effect, is also formed during the photo-oxidation of pentane.[9] In recent years, with the development of investigation method for EPS and the requirement of the green chemistry, various techniques have been developed to recycle and reuse it.[10] A great number of studies[11–16] focus on replacing pentane isomers with harmless blowing agents (such as water) for preparing EPS. To absorb water into the PS beads, the hydrophilic groups are introduced into the backbone of PS by copolymerizing,[17] such as ─OH group of starch.

As an inorganic blowing agent, water possesses the advantage of nonflammability, nontoxic, readily available, and inexpensive. However, the proportion of water entrapped in PS beads is very low and

having high boiling point, it is impossible to use the same procedure as the one used for pentane in preparing EPS. As a water absorbing material, starch can absorb much water and perform water-gel with high content water, especially with biodegradability, nonpollution to the environment, and safety during the processing. Starch has received considerable attention recently and been employed extensively in synthetic polymer, such as PS.[17–20] Starch is immiscible with most of the synthetic polymers, which can lead to agglomeration of the starch granules in a synthetic polymer matrix and poor performance of these materials. Better properties can be obtained through the introduction of compatibilizer between the two components.[21] Jan Pallay et al.[17] showed that the type of starch can influence the foam morphology of the pre-expanded copolymer beads. Up to now, no research focused on the effect of weight ratio of styrene/starch and styrene/water (O/W) on the properties of PS-starch copolymer with water blowing agent.

In this study, we prepare EPS with water (WEPS) instead of organic blowing agent. The starch is grafted onto PS-maleic anhydride (MAH) copolymer chains. The chemical structure and morphology of the copolymer are characterized. Furthermore, the water-swelling behavior and the thermal properties of copolymer are also investigated.

EXPERIMENTAL

Materials

The styrene monomer, MAH (99.5%), and soluble starch were purchased from Beijing Chemical factory, China. The initiators of dibenzoyl peroxide (BPO) and *tert*-butyl peroxybenzoate (TBPB) (99.5%) were obtained from Alfa Aesar Co. Tricalcium diphosphate, PVA, and Hydroxyethyl cellulose (HEC) were obtained from Xintuo Kemao Co., China.

Suspension polymerization

Suspension polymerization was performed in a four-hole boiling flask. BPO (0.025 wt % related to styrene) was dissolved in styrene (90 wt % of the total amount), then MAH and starch (0.5 wt % and 5 wt % related to total amount of styrene, respectively) were dispersed in the solution. The reaction mixture was heated to 120°C for prepolymerization under

TABLE I
Different O/W Ratio at Same Starch Content

	O/W ratio				
No.	1	2	3	4	5
O/W ratio	1 : 5	1 : 3	1 : 2	1 : 1.5	1 : 1.25

TABLE II
Different Content of Starch at Same O/W Ratio (1 : 1.5)

	Content				
No.	4	6	7	8	9
Starch/g	2.5	3	5	8	10
MAH/g	0.25	0.3	0.5	0.8	1
Content of starch/%	5	6	10	16	20

nitrogen atmosphere. The stirring rate was 350 rpm. After 1 h, the mixture was cooled to 60°C, then the styrene (10 wt % of the total amount) containing BPO and TBPB (0.375 wt % and 0.225 wt % related to the total amount of styrene, respectively) were added. Subsequently, water containing HEC and tricalcium diphosphate (0.075 wt % and 0.5 wt % related to water, respectively) were added in the mixture. The stirring rate was raised to 400 rpm. The temperature profile was as follows: 80°C for 240 min, 90°C for 120 min, and 120°C for 60 min, then the mixture was cooled to room temperature and the spherical beads were filtered and washed with water. The diameter of spherical beads is about 1 mm. The density of WEPS beads is about 1.08 g/cm^3. The O/W ratio and content of starch were changed as shown in Tables I and II, respectively.

Characterization

Infrared spectroscopic measurements were performed in the range 4000–400 cm^{-1} at a resolution of 4.0 cm^{-1} using a Bruker Tensor 27 FTIR spectrometer. Sample films were prepared by the spontaneous evaporation of a diluted. Gel permeation chromatography (GPC), GPC 1515 of the American Waters Co., was used to determine the average molecular weight and the molecular weight distribution (M_w/M_n) of WEPS. The morphology of beads was observed by field emission scanning electron microscope (FE-SEM, Hitachi S-4700, Japan). The T_g values were determined in the second ramp of the differential scanning calorimetry (DSC) diagram. The heating rate was 10°C/min from room temperature to 160°C under nitrogen. The thermal stability of WEPS was assessed by thermogravimetric analysis (TGA) using a TG 209 C analyzer operated at a heating rate of 10°C/min under a continuous flow of nitrogen from room temperature to 700°C. Foam morphology was measured by XSZ-H7 type phase-contrast microscope (Chongqing Opt-Eletri Co. China). The wavelength is 0.55 μm.

RESULTS AND DISCUSSION

FTIR analysis

Figure 1 shows the FTIR bands of 1776 and 1853 cm^{-1}, assigned to in-phase and out-of-phase stretching of
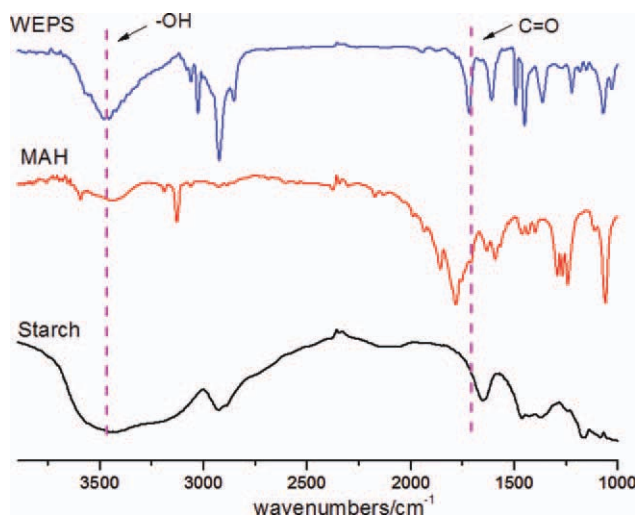
Figure 1 FTIR spectra of WEPS, MAH, and starch. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the carbonyl groups in the five-membered ring of MAH were not existed in starch-grafted PS-MA copolymer. While ─OH peak of starch at 3478.83 cm^{-1}, and C═O absorption peak at 1716 cm^{-1} both appeared. Hence, it indicated that starch was grafted on the PS and MAH copolymer chains. The chemical structure of WEPS scheme as followed Figure 2.

The use of starch with a very small granule size improved the foam morphology.[17] The granules tended to agglomerate once they were swollen with water. So, during the prepolymerization process, water should be excluded. MAH was easy to copolymerize with the monomer of styrene.[22] The hydroxyl of starch was to form H-bond with anhydride group of MAH on copolymer at prepolymerization process. Then the precopolymer was suspended in water, anhydride groups hydrolyzed into carboxylic acid, which could be graft copolymerized with the hydroxyl of starch (Fig. 2).[23]

Molecular weight and molecular weight distribution

The molecular weight and molecular weight distribution (or polydispersity index) at different O/W ratio and starch content were showed in Table III. At same content of the starch, the molecular weight of the copolymer increased as function of the O/W ratio, and the molecular weight distribution narrowed (Fig. 3). As nuclear agent at the beginning of the reaction, starch was surrounded by styrene monomer and MAH. The styrene was copolymerized with MAH with the proceeding of polymerization, and starch incorporated to MAH by hydrogen bond. With the increase of O/W ratio, starch gran-

ules were surrounded with higher concentration of styrene and MAH. When the reaction was performed in the bulk phase, the molecular weight of copolymer increased. Simultaneously, the monomer of MAH and styrene assembles around the starch particle uniformly, so it resulted in the narrow molecular weight distribution.

Figure 4 shows the relationship among the molecular weight, molecular weight distribution, and starch content at the same O/W ratio. The molecular weight of the copolymer decreased as a function of starch content. At the same time, the molecular weight distribution widened. The increased content of nuclear agent starch results the higher degree of agglomeration, the amount of monomer around it
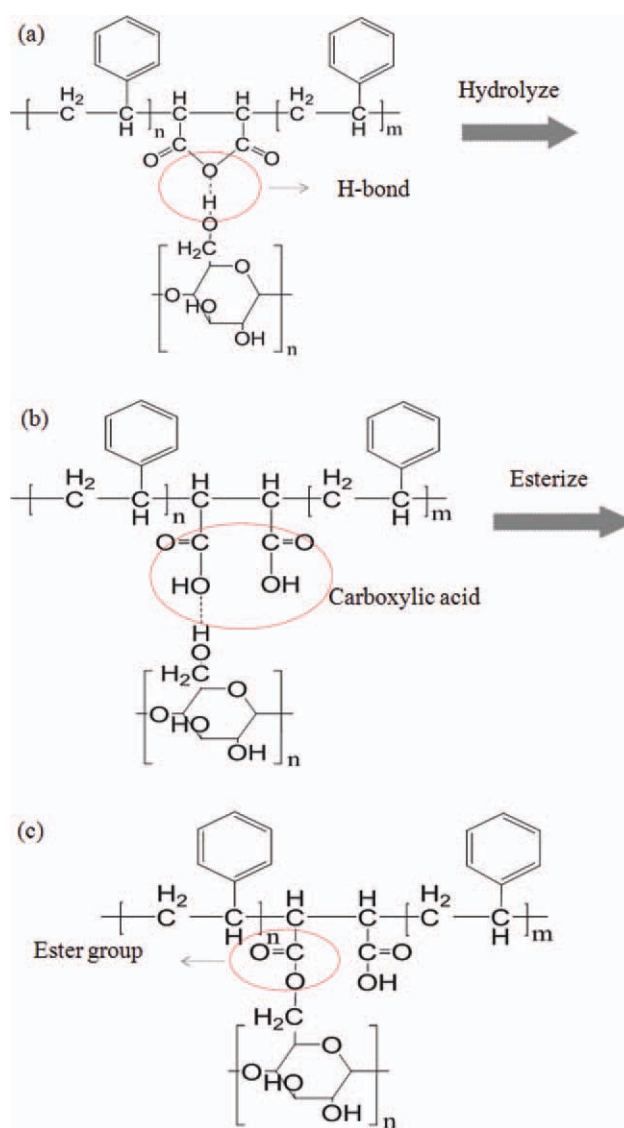

Figure 2 The chemical structure scheme of the copolymer in different polymerization cycles (a) prepolymerization; (b) suspension polymerization; and (c) polymerization process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Molecular Weight and Molecular Weight Distribution of WEPS

No.	O/W ratio	Starch (g)	T_g (°C)	M_n (g/mol)	M_w (g/mol)	Polydispersity index
1	1 : 5	2.5	99.6	62,565	1,29,948	2.077
2	1 : 3	2.5	101.1	57,155	1,23,475	2.16
3	1 : 2	2.5	97.3	63,466	1,25,230	1.973
4	1 : 1.5	2.5	97.2	98,429	1,74,223	1.77
5	1 : 1.25	2.5				
6	1 : 1.5	3	98.1	80,464	1,54,680	1.922
7	1 : 1.5	5	102.7	73,489	1,50,378	2.046
8	1 : 1.5	8				
9	1 : 1.5	10				

declined, and the ununiformly assembles around the starch particle.

DSC analysis

The DSC thermograms were given in Figure 5. All of the copolymers showed the single T_g. The increase in the T_g values with an increase of starch and MAH content was expected. Because the hydrophilic property of starch facilitated the fixation of water within the beads, the water absorbed by the granules increased the mobility in the amorphous domains, leading to realignment and formation of new intermolecular bonds.[24] Overall, it leaded to an additional enthalpy bonus, which was not directly related to crystallinity.[25] Furthermore, much more starches were grafted onto the backbone of copolymer, and the density of hydrogen bond interaction was also enhanced, which retarded the movements of PS chain segments.

Thermogravimetric analysis

The amount of water (blowing agent) incorporated in the starch of copolymer was evaluated with TGA (Fig. 6). It was expected that the weight loss of copolymer increased dramatically as function of the O/W ratio in the range of 100–200°C, which was caused by the loss of water. It indicated that the content of water was high in the WEPS copolymerized at high O/W ratio. The water content was determined by the content and structure of the starch in the copolymer. Under higher O/W ratio, starch was surrounded by more styrene. With the development of the polymerization, the viscous reaction mixture was easy to fixate more water in the droplets and form intramolecular H-bond with starch until the polymerization finished. At the same O/W ratio, more starch and MAH were added into the reaction, the water content increased at first then decreased [Fig. 6(b)]. Starch molecules with much ─OH groups were easy to form intermolecular or intramolecular H-bond with the increasing of starch content, thus water molecules formed H-bond with starch molecules from easy to difficult. Especially at the concentration of starch changed from suitable to excessive, it was easy for self-aggregation of starch. The results showed that the 6 wt % starch absorbed the maximum water, which was higher than that of 5 wt % and 10 wt % starch content, respectively. In addition, the weight loss of second stage increased with the increasing of the starch content, which also indicated the increased starch content in the copolymer.
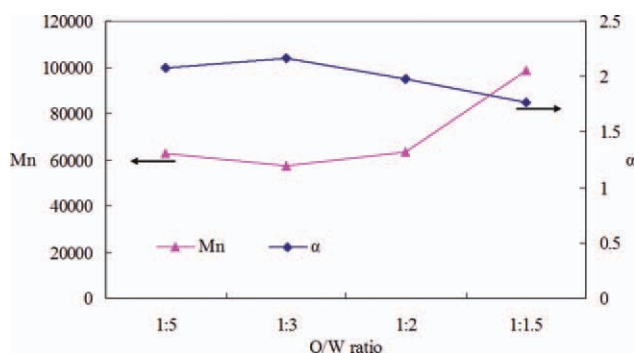

Figure 3 Molecular weight and molecular weight distribution (α) at different O/W ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
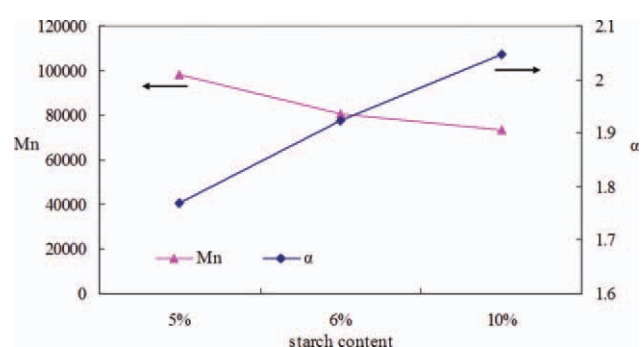

Figure 4 Molecular weight and molecular weight distribution (α) at different starch content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
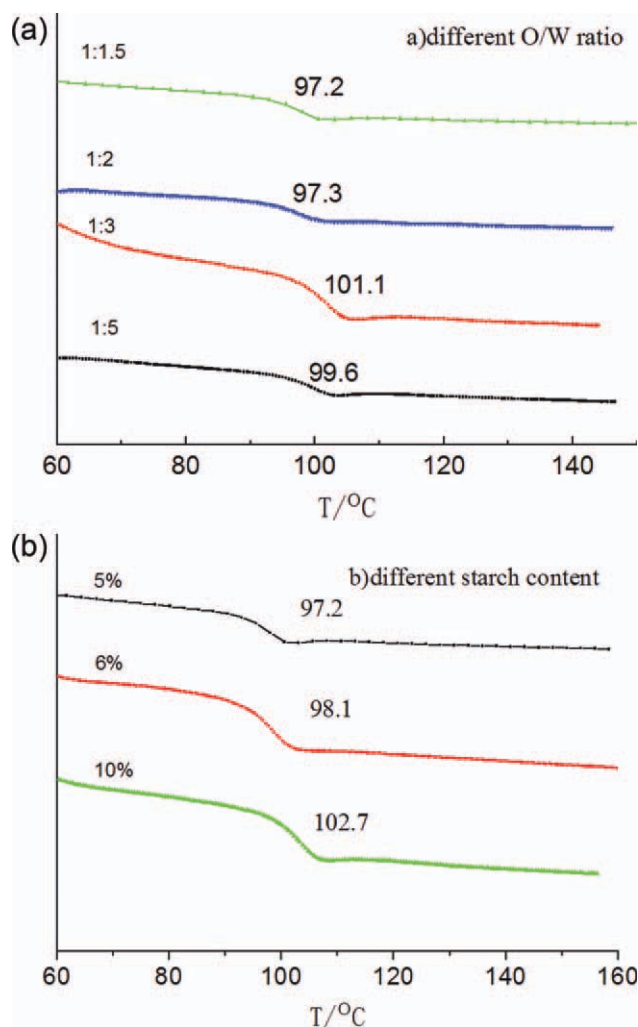
Figure 5 T_g of WEPS varied with (a) different O/W ratio and (b) different starch content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 Water and starch loss of WEPS which synthesized in (a) different O/W ratio and (b) different starch content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scanning electron microscopy

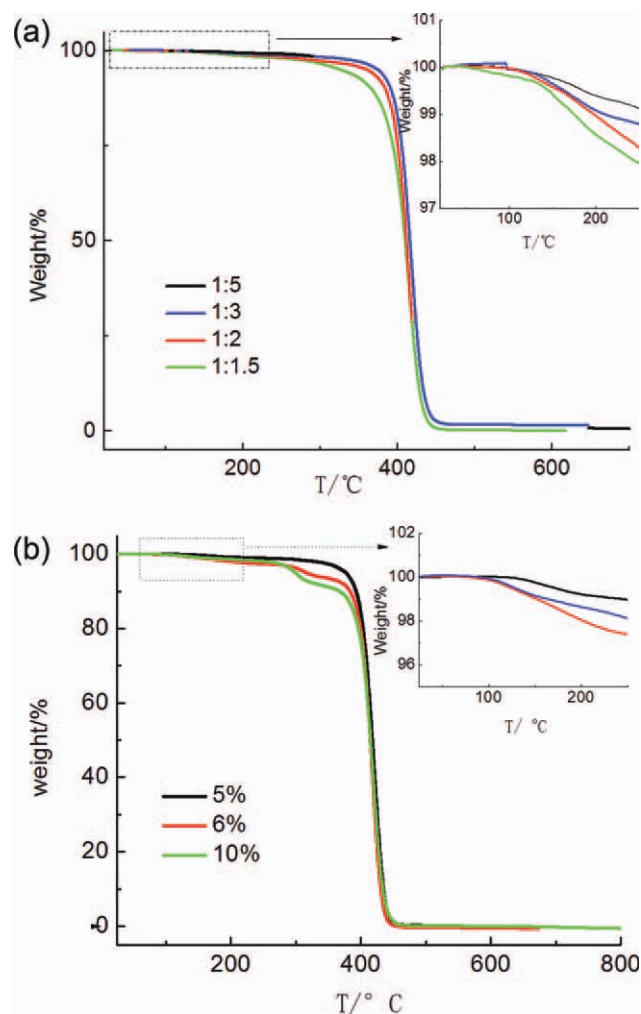To prepare the foam with good thermal and mechanical properties, the key factor is to create small and monodisperse foam. This implied the preparation of compact (before expansion) WEPS beads containing small water droplets with a narrow size distribution. Therefore, the establishment of a suitable morphology was of crucial importance. The ultimate bead size was mainly determined during suspension
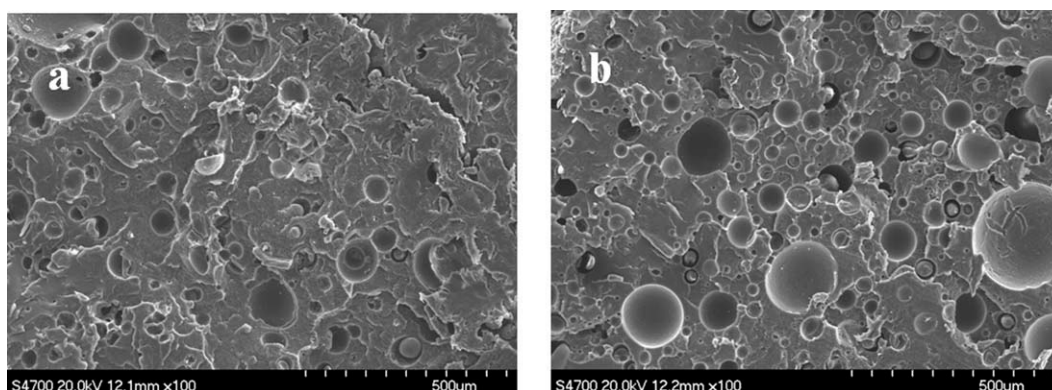

Figure 7 Starch riched phase of WEPS in (a) 5 wt % starch content and (b) 6 wt % starch content.
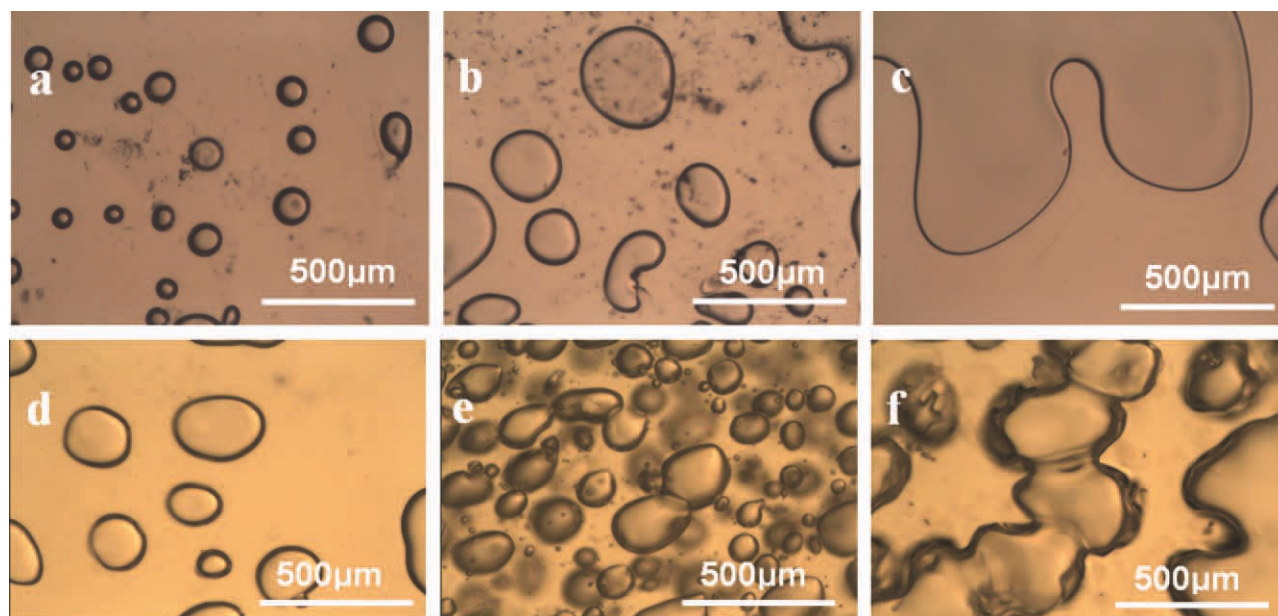
Figure 8 Water bubbles distribution of WEPS observed on optical microscope at different O/W ratio: (a) O/W ratio = 1 : 5, (b) O/W ratio = 1 : 3, (c) O/W ratio = 1: 2 and at different starch content: (d) 5 wt %, (e) 6 wt %, (f) 10 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerization. It could be controlled by a number of means including stirring rate, the type and content of stabilizers, dispersants, and starch. For WEPS synthesis in this study, the bead size fell in the range of typical group at same starch content, but in the range of the large group as a function of starch content.

The copolymer phase structure in compact beads presented in Figure 7 and the different domain size and size distribution of phase structure were obtained for WEPS with different starch content. Most domains were spherical and exhibited a size of about 50 μm, with several larger domains of ~ 200 μm, which was water-swelled starch-grafted copolymer. At 6 wt % of starch content, the domain size distribution was more uniform. Some larger domains indicted that swelled starch tended to agglomerate.

Optical microscope

The microfoam morphology of the copolymer was also investigated by optical microscope. Figure 8 shows optical micrographs of starch-grafted WEPS with different O/W ratio and starch content as heated up to 200°C. It was obviously visible that the two-phase structure was presented in starch-grafted copolymer. Starch molecules were trend to self-assemble to form different size starch phase which can absorb water. When the matrix was heated, the water absorbed in the starch evaporated into steam, then formed the steam bubbles in the copolymer. With the increase of O/W ratio, the water bubble size increased. With the increase of starch content,

the bubble size distribution was more uniform. This result was consistent with the TGA data.

CONCLUSIONS

The WEPS beads were prepared by using the suspension polymerization process. O/W ratio and starch content affected strongly the properties and morphology of WEPS. With the increase of O/W ratio, the water content, molecular weight, and phase domain size increased, and the molecular weight distribution and the T_g value of copolymer both decreased. With the increase of starch content, molecular weight distribution and the T_g of the WEPS both increased, and the molecular weight decreased. The water content in the beads reached the maximum value and the starch phase distribution reached the most uniform at 6 wt % of starch at same O/W ratio.

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