Effect of Reaction Conditions on Grafting Ratio and Properties of Starch Nanocrystals-g-polystyrene

Cai Wang, Zelin Pan, Meiyan Wu, Ping Zhao

Beijing National Laboratory for Molecular Sciences (BNLMR), Key laboratory of Green Printing, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100190, China
Correspondence to: C. Wang (E-mail: wangc@iccas.ac.cn)

ABSTRACT: Starch nanocrystals-g-polystyrene (StN-g-PS) was synthesized by free radical emulsion copolymerization of starch nanocrystals with styrene. The effect of polymerization conditions on grafting efficiency (GE) and grafting ratio (GR) were investigated. It was found that during graft copolymerization procedure both GE and GR increase with increasing monomer concentration and reaction time. As a result the high GE and high GR can be achieved. The good linear fit of the GR with A_{St}/A_{OH} (the absorption strength ratio of aromatic ring peaks and hydroxyl group peaks) confirmed that during graft copolymerization, FTIR spectra can be used as a simple method for determining GR. X-ray diffraction showed that the crystallinity of StN-g-PS decreased slightly with increasing GR. Grafted polystyrene side chains can improve the interface compatibility of starch nanocrystals with the hydrophobic polymer matrix. The mechanical properties of StN-g-PS/rubber nanocomposites can be obviously enhanced. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40571.

INTRODUCTION

Starch is a cheap, renewable and natural biodegradable polymer. Native starch occurs in the form of discrete and semicrystalline microstructure consisting of amorphous and crystalline phases. Starch nanocrystals resulting from the disruption of amorphous part is usually prepared by the acid hydrolysis of native starch using hydrochloric acid or sulfuric acid.[1,2] They consist of crystalline nanoplatelets about 5–7 nm thick with a length of 20–40 nm and a width of 15–30 nm.[1]

Recently, a growing interest in varied modified starch nanocrystal derivatives has been reported.[3] Most of them are esters of starch nanocrystals and obtained through the reactions with hydroxyl groups of starch, for instance, the octanoyl starch nanocrystals,[4] nonanoyl starch nanocrystals,[4] decanoyl starch nanocrystals,[4] acetylated starch nanocrystals,[5] starch nanocrystals-g-polycaprolactone,[6,7] the crosslinking modified starch nanocrystals,[8,9] and so on.

The use of starch nanocrystals as reinforcing agents in polymer composites led to a desirable reinforcing effect.[3] Starch nanocrystals derivatives can be used in different polymer matrix, such as natural rubber,[10–12] thermoplastic starch,[13] poly(lactic acid),[14] poly(butylenes succinate),[15] waterborne polyurethane,[6,16,17] carboxymethyl chitosan,[18] and so on. Angellier et al.[10] reported starch nanocrystals as green fillers of natural rubber. However, when the content was above 20 wt %, the reinforcing effect decreased instead. This is because the hydrophilicity of starch nanocrystals, attributed to abundant hydroxyl groups, decreases the interface compatibility between hydrophilic starch nanocrystals and hydrophobic rubber matrix.

For improving the hydrophobicity of starch nanocrystals and enhancing its compatibility with polymer matrix, a starch nanocrystals-g-polystyrene (StN-g-PS) by free radical polymerization in emulsion was synthesized in our laboratory as we reported previously.[19] The graft copolymerization of native starch with varied monomers and the influence factors on reaction, such as initiator, monomer concentration, reaction temperature, and time have been studied.[20–25] However, the graft polymerization of styrene onto a nanoscale starch has less been studied. In this article, the effect of reaction conditions on grafting efficiency (GE), grafting ratio (GR), the grafting sites on starch backbone, as well as the properties of graft copolymers as a new nanosize filler are investigated.

EXPERIMENTAL

Materials

Corn starch with water content 14% is the product of Beijing Hongxing starch Company, China. Styrene, the product of

Tianjin No 1 chemical reagent factory and used as received. Potassium persulfate (KPS), sodium dodecylbenzene sulfonate (SDBS), sulfuric acid, acetone, sulfur, and toluene were all of analytical grade, produced by Beijing chemical reagent company. Natural rubber latex was provided by Beijing Bolide Trading Company of China, with a solid content 40%. Distilled water was used for graft copolymerization.

Preparation of Starch Nanocrystals-g-polystyrene

Starch nanocrystals were prepared by acid hydrolysis of native starch according to Angellier et al.[2] Corn starch powder (36 g) were mixed with 250 mL of 2.87 mol L^{-1} sulfuric acid solution. The suspensions were placed at 45°C hydrolyzed for 7 days under constant stirring, then repeatedly washed by distilled water and separated by successive centrifugations until neutrality. The dispersion of starch nanocrystals in water was completed by a further 5-min ultrasonic treatment. Emulsion polymerization was conducted in a 250-mL three-neck flask equipped with a condensation tube and the water bath. Under continuously stirring, 100 g starch nanocrystals dispersion (containing 3 g of starch nanocrystals based on dry weight), settled mass of styrene [according to the molar ratio (MR) of monomer and starch nanocrystals], 30 mg of NaHCO$_3$ were added to the flask, respectively, and under atmosphere N$_2$ for 10 min at 40°C (bath temperature). Then, 40 mg of SDBS and KPS (0.5% on the mass of styrene) were added. The reaction mixture was heated to 70°C. Samples were taken, respectively, at the reaction time 5, 8, 10, and 12 h. Several drops of acetone were added into the obtained samples under stirring. The graft copolymer was separated from emulsion by successive centrifugation and washed with distilled water. The polystyrene homopolymer as byproduct was separated from graft copolymer by Soxhlet extraction with toluene for 24 h. Then the purified graft copolymer was dispersed in ethanol to get the emulsion of StN-g-PS.

Preparation of StN-g-PS/Natural Rubber Nanocomposites

The dispersion liquid StN-g-PS was mixed with natural rubber latex, and stirred vigorously for 50 min at room temperature. A few drops of acetone were used to coagulate the mixture. The coagulated mixture was thoroughly washed with water and then vacuum-dried at 60°C for 8 h until water contents lower than 0.5%. The dried natural rubber or StN-g-PS/natural rubber blends was mixed with the vulcanizing agent and other additives by a rubber fining mixer (two-roll mill) at 50–60°C by flowing procedure: first of all, the accelerator N-(oxidiethylene)-2-benzothiazolyl sulfenamide [0.8% (based on the mass of natural rubber), this were provided by Beijing tyre Company of China] was added and then the rubber process oil (aromatic hydrocarbon oil) [5% (based on the mass of natural rubber, this were provided by Beijing tyre Company of China)] and finally the vulcanizing agent [sulfur 1.2% (based on the mass of natural rubber)] was added. The mixing time was 7–8 min. The mixed rubber nanocomposites sheet was placed in a tablet compressing mold, the vulcanization was performed on a flat vulcanizing machine at pressure 10 MPa, temperature 150°C for 10 min. The mechanical properties of vulcanized rubber samples were tested after placing 6–12 h.

Materials Characterization

^{1}H-NMR spectra of starch nanocrystals and StN-g-PS was recorded on a Bruker AV400 spectrometer (Bruker AXS, Germany) at room temperature using DMSO-d_6 or DMSO-d_6/CDCl$_3$ as solvents and tetramethylsilane as an internal reference.

FTIR spectra in the range of 4000–400 cm^{-1} were recorded on FTIR TENSOR 27 spectra (Germany BRUKER). KBr pellet was used for sample preparation. The change of the absorption strength ratio of aromatic ring and hydroxyl was investigated.

The XRD patterns of starch nanocrystals before and after graft modification were obtained on Rigaku D/max-2500 X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu-Kα radiation at 40 kV and 200 mA. The diffraction data were recorded over the 2θ range of 3–40°.

The morphology of starch nanocrystals and StN-g-PS were observed by scanning electron microscope (SEM Japan Hitachi, S-4300F) with the highest distinguishability of 1.5 nm. The sample surface was first coated with a thin layer of gold.

Contact angle experiment was conducted to evaluate the affinity to water of the StN-g-PS. Dry StN-g-PS powder was dispersed in DMSO, and then spread uniformly on glass. Films were gotten under heating for 12 h before being tested on a contact angle meter OCA20 Micro (Data-Physics, Germany). Three drops of water were placed successively on different parts of a film, and their left and right angles were measured. The value reported is the average of six measurements.

The mechanical properties were tested on universal tensile tester (CMT 4104 Electrical Tensile Instrument, Shenzhen SANS Test Machine, China) at 500 mm min^{-1}. The dumbbell-shaped specimens were used. At least five specimens were tested for an average value.

Determination of Grafting Parameters

The MR of grafted polystyrene unit and glucose unit in StN-g-PS, the GR, and the GE were calculated as follows:

$$MR = \frac{(W_1 - W_0) \times 162}{W_0 \times 104} \quad (1)$$

$$GR(\%) = \frac{W_1 - W_0}{W_0} \times 100 = \frac{MR \times 104}{162} \times 100 \quad (2)$$

$$GE(\%) = \frac{W_1 - W_0}{W_2} \times 100 = \frac{MR}{(S/SN)} \times 100 \quad (3)$$

where W_0, W_1, and W_2 denote the weights of the original starch nanocrystals, grafted starch nanocrystals, and the styrene monomer used, respectively. S/SN denotes the MR of styrene monomer and glucose unit in starch nanocrystals.

In this article, the GE and also the GR are further evaluated by ^{1}H-NMR spectrum. According to ^{1}H-NMR spectrum, the chemical shifts at 3.7, 4.6, 5.1, and 5.6 ppm correspond to the nonhydroxyl protons (-CH-, -CH$_2$-) in glucose unit of starch, at 6.7 and 7.1 ppm are the protons absorption peaks of aromatic ring. Thus, the MR of grafted polystyrene unit and glucose unit in graft copolymer (MR) can be calculated by the equation MR= $(I_a/5)/(I_b/2)$, where I_a was the intensity of the peaks corresponding to the aromatic ring protons (I_a) at 6.7 and 7.1 ppm, and I_b was the intensity of the peaks corresponding to proton (-CH-) of glucose unit at 5.6 ppm.

From MR values obtained, the GE and the GR can be easily calculated. The values obtained by mass method are in good accord with the values determined by ^{1}H-NMR spectrum.
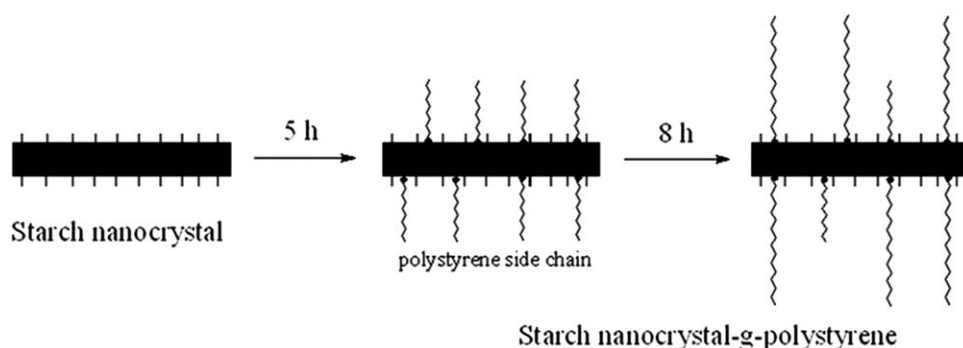
Figure 1. Process of graft copolymerization of styrene onto starch nanocrystals.

RESULTS AND DISCUSSION

Effect of Reaction Conditions on Grafting Ratio

Graft copolymerization of styrene onto starch nanocrystals was conducted in emulsion by free radical mechanism. The characterization of the graft copolymer obtained has been reported by the authors.[19] The graft polymerization mainly occurs at the surface of starch nanocrystals. During grafting course after initiation, the polystyrene grafted chain length increases with increasing reaction time. As it schematically indicated in Figure 1, at 8 h reaction time, polystyrene side chain length is much longer than that of at 5 h.

In general, during the graft copolymerization by free radical mechanism the homopolymers always occur at the same time with the graft copolymers formation. Therefore, the graft efficiency (GE) is important in evaluation of a graft copolymerization. GE means how many monomers are consumed in graft chain formation. GE can be calculated in two ways. One is based on the conversion % of monomer. The other is based on the monomer used. Obviously, at the same condition, the GE value calculated based on monomer mass is lower than that on monomer conversion, as the monomer conversion was not

100%. In this paper the GE was calculated based on the monomer added.

GR is another important parameter, which is to describe the graft chain contents in graft copolymers obtained. GR tightly concerns the properties of the graft copolymers obtained.

It was found that the concentration of styrene monomer (the MR, denotes as S/SN), the reaction time and the initiator concentration strongly affected the GE and the GR of the graft copolymerization.

Firstly, as the initiator concentration keeps constant (0.5% based on styrene) the effect of reaction time and monomer concentrations on the GE and GR were studied. Results were illustrated in Table I. As it can be seen from Table I, the GR and GE both increased with increasing monomer concentration (S/SN) and with reaction time. As a result high GR and GE can be achieved with increasing reaction time. The GR values increased with increasing monomer concentration (S/SN) and reaction time were also indicated in Figure 2. Clearly, the graft polymerization depends on the availability of styrene monomers in the vicinity of starch macromolecule.[24] The probability of collision between monomer molecules and starch macromolecules increased when the concentration of styrene monomer increased.

A lot of graft copolymers of native starch with varied monomers have been studied, styrene was thought to be the relatively

Table I. Effect of Monomer Concentration and Reaction Time on Starch Nanocrystals-g-polystyrene Copolymerization

Samples	S/SN	Reaction time (h)	MR	GR (%)	GE (%)
A1		5	0.01	0.64	2
A2		8	0.03	1.93	6
A3	0.5	10	0.045	2.89	9
A4		12	0.05	3.21	10
B1		5	0.10	6.42	10
B2		8	0.28	17.98	28
B3	1.0	10	0.52	33.38	52
B4		12	0.63	40.44	63
C1		5	0.17	10.91	11.3
C2		8	0.33	21.19	22
C3	1.5	10	0.83	53.28	55.3
C4		12	0.89	57.14	59.3

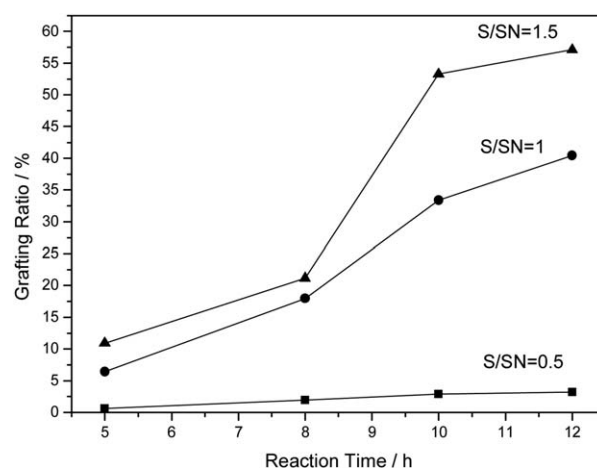Initiator concentration is 0.5% (based on the mass of styrene).

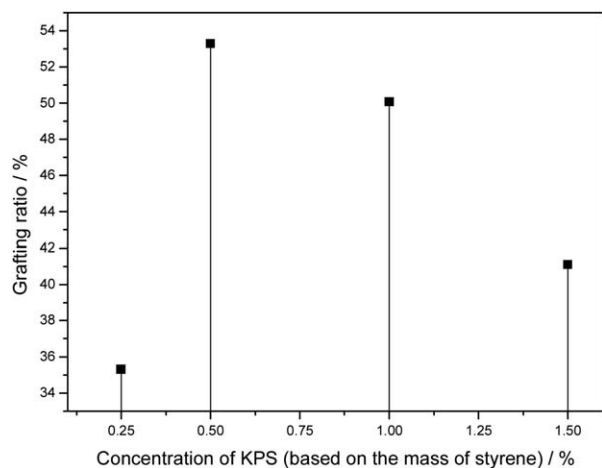**Figure 2.** Effect of monomer concentration (S/SN) and reaction time on grafting ratio.

Figure 3. Effect of initiator concentration (based on the mass of styrene) on GR.

Figure 5. The change of the ratio A_{St}/A_{OH} with GR.

inactive monomer to starch.[23] In this article the starch nanocrystals with the size around 20–50 nm was used instead of the native starch and the high GE can be achieved. It can be explained that according to the thermodynamic principle, reducing the size of macromolecules its miscibility with monomer will be increased, as the variation of entropy ΔS increases and also possibly increasing the interfacial area.

As the same reason, the grafting reactions occurring between two macromolecules having great difference in polarities are not likely. Therefore, even the nanoscale starch is used instead of native starch, the grafting of the growing polystyrene free radicals from micelles onto starch are not effective in competing with that of styrene monomer.

Emulsion polymerization is a rather complex process, Imagining that once the graft copolymer occurs in emulsion, the amphiphilic characters of the starch nanocrystals-g-styrene graft copolymer may play an additional stabilize effect to prevent the interactive latex particles from coagulation. All these factors
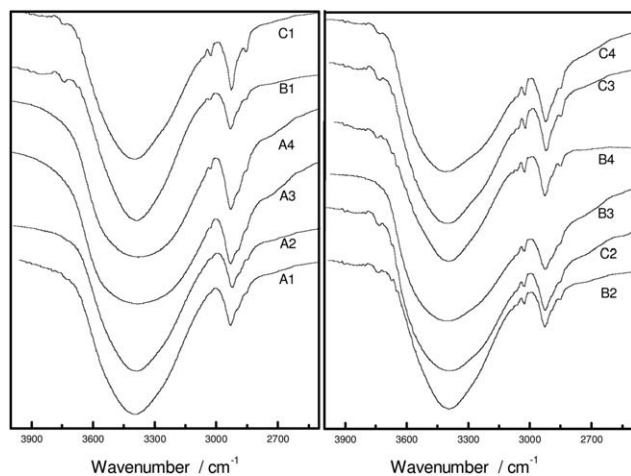
may improve the graft copolymerization of starch nanocrystals with styrene.

In this reaction system the water soluble initiator was used. The effect of initiator concentration on GR and GE was studied at the reaction condition that S/SN was 1.5 and reaction time was 10 h. The data obtained were shown in Figure 3.

With increase of initiator concentration, GR first increased then decreased. GR reached the maximum at initiator concentration 0.5%. This is due to the fact that in the region of low initiator concentration, the active sites on starch macromolecules increased with increasing initiator concentration, and GR increased accordingly. However, when initiator concentration is higher than 0.5%, the homopolymerization of styrene became the leading factor, resulting in decrease of GR.

FTIR Spectra Analysis of StN-g-PS with Different GR

It was known that the graft copolymerization of polystyrene occurred on the surface of the starch nanocrystals. However, the grafting site on starch is still not elucidated. One hypothesis in
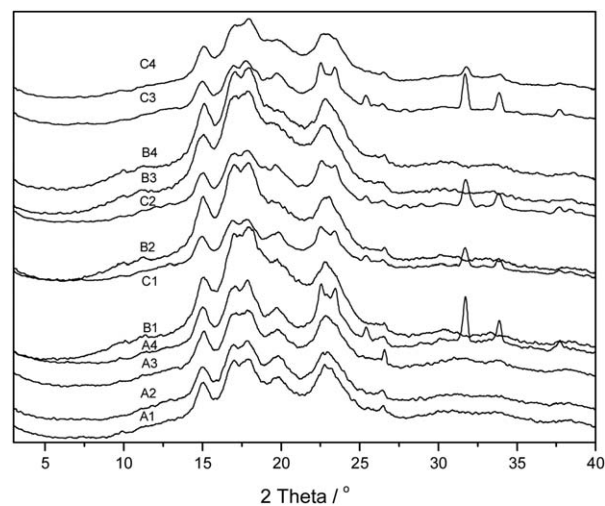

Figure 4. FTIR spectra of starch nanocrystals-g-polystyrene with different GR.

Figure 6. XRD patterns of starch nanocrystals-g-polystyrene with different GR.
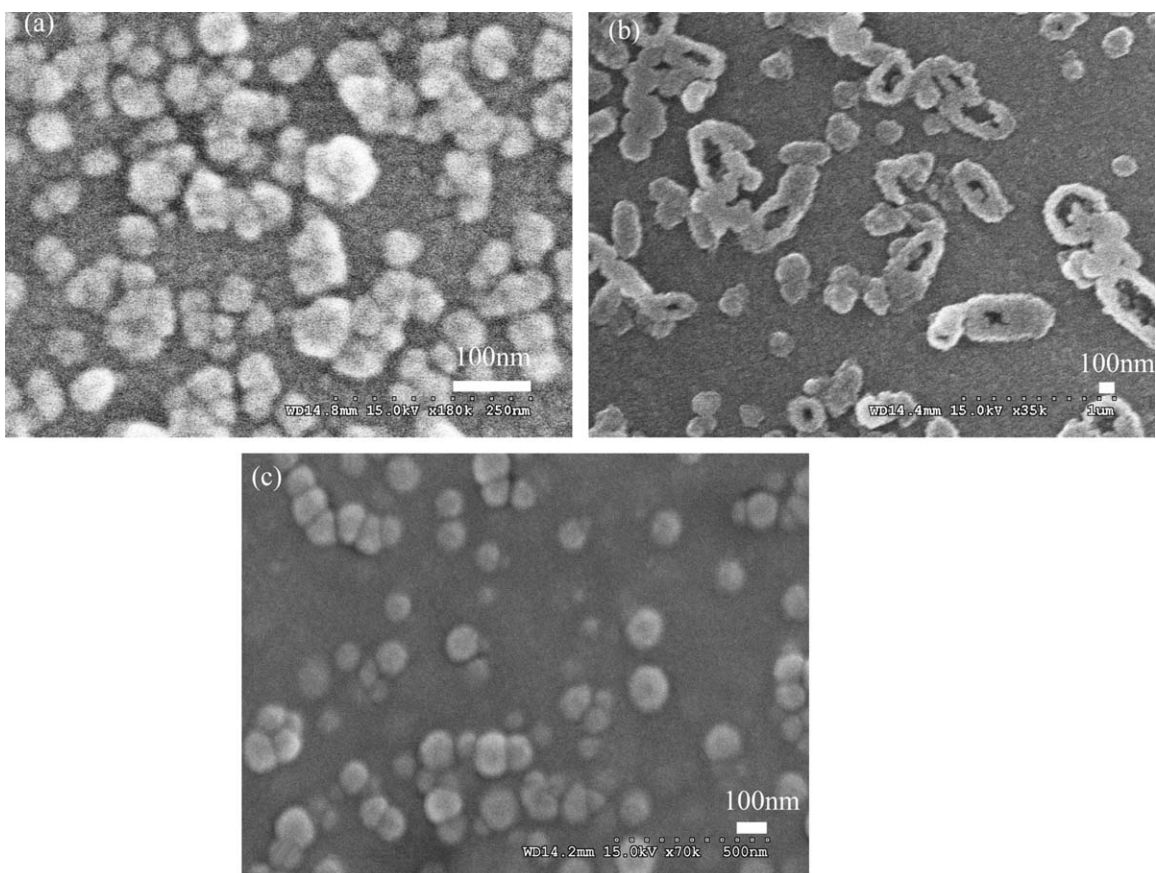
Figure 7. Morphologies of starch nanocrystals and starch nanocrystals-g-polystyrene of different reaction time (a) Ungrafted starch nanocrystals, (b) StN-g-PS sample B1 of 5 h, GR 6.42%, and (c) StN-g-PS sample B2 of 8 h, GR 17.98%.

literature is that an oxy radical may be formed from OH groups on the surface of starch. The grafting occurs by the copolymerization of styrene onto oxy radicals.[23]

The presence of OH groups in grafted copolymers and the change with graft polymerization process were investigated by FTIR. The FTIR spectra of graft copolymers StN-g-PS with various GR% were shown in Figure 4. The absorption at 3392 cm^{-1} is designated as OH groups of starch; the absorption of polystyrene aromatic ring locates at 3027 cm^{-1}. As it can be seen that the absorption peaks at 3027 cm^{-1} increase obviously with increasing GR while the OH absorption peaks at 3392 cm^{-1} almost do not change.

All samples A1-A4, B1-B4, C1-C4 obtained at varied reaction conditions listed in Table I. Therefore, the ratio of the absorption strength of the two peaks A_{St}/A_{OH} against the GR is plotted and shown in Figure 5. Here, the A_{St} and A_{OH} denote the absorption strength contributed by grafted polystyrene and OH groups of starch, respectively.

As indicated in Figure 5, the ratio A_{St}/A_{OH} increased linearly with increasing GR. The good linear fit of the GR with A_{St}/A_{OH} confirmed that during the graft copolymerization, FTIR spectra can be used as a simple method for determining GR. At very low GR%, as the first four points in Figure 5, , a variance to linear fit was observed. This is because the

accuracy of the infrared spectrum is not enough as the content is low.

X-ray Diffraction Analysis of StN-g-PS with Different GR
The X-ray diffraction powder patterns of StN-g-PS with different GR were shown in Figure 6. Compared with the typical diffraction peaks of starch nanocrystals, which at 2θ 15°, 17°, 18°, 20°, and 23°,[19,26] the corresponding main diffraction peaks of
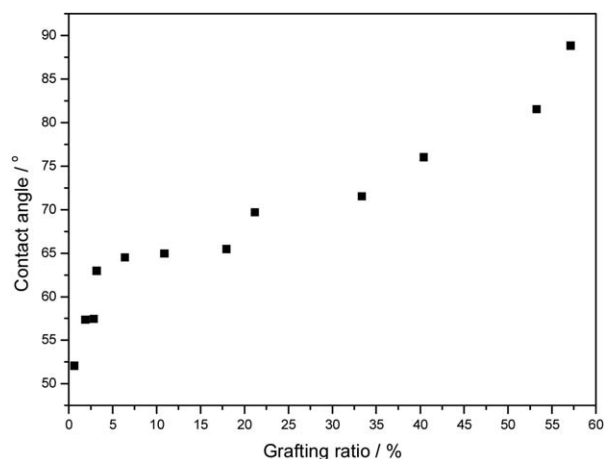

Figure 8. The variation of contact angle with GR.

Table II. Mechanical Properties of StN-*g*-PS/Natural Rubber Nanocomposites

	NR[a]	StN-1[a]	StN-2[a]	GStN-1[a]	GStN-2[a]
StN (% in weight)	0	5	15	0	0
StN-*g*-PS (% in weight)	0	0	0	5	15
Shore A hardness	18	20	21	18	26
Modulus at 100% elongation (MPa)	0.16	0.19	0.26	0.27	0.36
Modulus at 300% elongation (MPa)	0.17	0.20	0.40	0.24	0.48
Tensile strength (MPa)	0.25	0.33	0.50	0.83	1.55
Elongation at break (%)	953	915	748	951	699

NR, nature rubber; StN, ungrafted starch nanocrystals; StN-1, StN-2, nanocomposites of NR with starch nanocrystals; GStN-1, GStN-2, nanocomposites of NR with StN-*g*-PS.
[a] The details in recipe and preparation process see Experimental section "Preparation of StN-*g*-PS/nature rubber nanocomposites".

StN-*g*-PS were at 2θ 15°, 17°, 18°, and 23°, indicating that modification had almost no influence on the crystalline structure of starch nanocrystals. Meanwhile, the diffraction peak of polystyrene at 2θ 20° gradually weakened with increasing GR These phenomena can be attributed to the coating of starch nanocrystals with a grafted polystyrene layer. The grafted polystyrene chains arrange irregularly on the polysaccharides backbones and are no crystallization.[19] The crystallinity of StN-*g*-PS decreased slightly with increasing GR.

Effect of Reaction Time on Morphology of Starch Nanocrystals-*g*-Polystyrene
In order to further study the effect of reaction conditions on graft copolymers obtained the morphology of two StN-*g*-PS samples of different graft copolymerization reaction time were studied by scanning electron microscope (SEM) and shown in Figure 7. Sample B1 has reaction time of 5 h, and sample B2 is 8 h. At initial grafting stage the polystyrene graft side chain is relatively short and it becomes longer with reaction time (as it schematically indicated in Figure 1). Sample B1 of 5 h has shorter polystyrene side chains and lower GR of 6.42%. As it can be seen in Figure 7(b), its morphology shows an irregular flake structure, but with a thick edge. In this case, the surface of starch nanocrystals is partially masked with short grafted polystyrene chains. Along with increasing reaction time up to 8 h (sample B2), the grafted polystyrene side chains become longer and GR increased to 17.98%. The hydrophobic side chains may fully covered the surface of starch nanocrystals and makes it into nearly spherical particles [Figure 7(c)].

Contact Angle Measurements
The contact angle measurements were carried out by depositing a drop of distilled water onto the surface of a StN-*g*-PS film. The change of contact angle with GR was shown in Figure 8.

It can be seen from Figure 8 that ungrafted starch nanocrystals have the smallest contact angle showing a good hydrophilicity. This is because a plenty of hydroxyl groups present on the surface of starch nanocrystals. The graft copolymer StN-*g*-PS became more hydrophobic, when the starch surface was covered with grafted hydrophobic polystyrene chains. The contact angle of StN-*g*-PS increased with increasing GR as the hydrophobicity increased. Increasing hydrophobicity of modified starch nanocrystals is obviously can improve its interface compatibility with hydrophobic nature rubber (NR).

Mechanical Properties of StN-*g*-PS/Nature Rubber Nanocomposites
In order to explore the reinforcing function of StN-*g*-PS to nature rubber (NR), the rubber nanocomposites were prepared by mixing the natural rubber latex with liquid dispersion of StN-*g*-PS and, for comparison, also with that of starch nanocrystals (StN), and then vulcanized. Sample B2 of GR 17.98% was used as StN-*g*-PS. The mechanical properties of the rubber nanocomposites with StN-*g*-PS of 5% (GStN-1) and 15% (GStN-2), respectively, are compared with the rubber nanocomposites with StN of the same contents and the NR as a blank. Results obtained are listed in Table II.

Note, the data in Table II are for relative comparison. Since in experiments except nanostarch as green filler, other reinforcing fillers such as carbon black were not added; in addition, the aromatic hydrocarbon oil 5% was added as rubber process additive. Both factors led to depress the mechanical properties of samples, but not influence these data using as relative comparison, because all samples were prepared at the same conditions.

As It can be seen from Table II, when the addition of StN-*g*-PS from 5% up to 15% the hardness, modulus, and tensile strength of the rubber composites with StN-*g*-PS (GStN-2) are remarkably enhanced, and are better than that with StN-2 of the same contents, in particular, the tensile strength of GStN-2 increased five times as compared with StN-2, and six times compared with NR. This is because, as indicated by contact angle, the StN-*g*-PS having enhanced hydrophobicity and thus improved interface compatibility with rubber matrix results in improved mechanical properties. It reveals that StN-*g*-PS is an effective green reinforcing nanofiller to NR.

CONCLUSIONS

The StN-*g*-PS was prepared by emulsion free radical graft copolymerization, since the nanostarch was used instead of native starch, the high GE and the high GR can be achieved. During emulsion polymerization the GE and GR increase with increasing reaction time and monomer concentration, while the initiator concentration shows a top value, high this value, GR decreases. FTIR spectra can be used as a simple method for determining GR.

It is found that the morphology of StN-*g*-PS changes with the samples taken at different reaction time (different GR, different polystyrene side chain length).

The contact angle measurements indicated that hydrophobicity of StN-*g*-PS increased with increasing GR. Due to enhancing hydrophobicity, the StN-*g*-PS showed an excellent reinforcing function to hydrophobic rubber matrix. When 15% StN-*g*-PS of GR 17.98% was taken as a green nanofiller to blend with NR, the mechanical properties of the rubber composites obtained can be remarkably improved.

REFERENCES

1. Putaux, J. L.; Molina-Boisseau, S.; Momaur, T.; Dufresne, A. *Biomacromolecules* **2003**, *4*, 1198.

2. Angellier, H.; Choisnard, L.; Molina-Boisseau, S.; Ozil, P.; Dufresne, A. *Biomacromolecules* **2004**, *5*, 1545.

3. LeCorre, D.; Bras, J.; Dufresne, A. *Biomacromolecules* **2010**, *11*, 1139.

4. Namazi, H.; Dadkhah, A. *Carbohydr. Polym.* **2010**, *79*, 731.

5. Xu, Y.; Ding, W.; Liu, J.; Li, Y.; Kennedy, J. F.; Gu, Q.; Shao, S. *Carbohydr. Polym.* **2010**, *80*, 1078.

6. Chang, P. R.; Ai, F.; Chen, Y.; Dufresne, A.; Huang, J. *J. Appl. Polym. Sci.* **2009**, *111*, 619.

7. Namazi, H.; Dadkhah, A. *J. Appl. Polym. Sci.* **2008**, *110*, 2405.

8. Ren, L.; Jiang, M.; Wang, L.; Zhou, J.; Tong, J. *Carbohydr. Polym.* **2012**, *87*, 1874.

9. Jivan, M. J.; Madadlou, A.; Yarmand, M. *Food Chem.* **2013**, *141*, 1661.

10. Angellier, H.; Molina-Boisseau, S.; Lebrun, L.; Dufresne, A. *Macromolecules* **2005**, *38*, 3783.

11. Mele, P.; Angellier-Coussy, H.; Molina-Boisseau, S.; Dufresne, A. *Biomacromolecules* **2011**, *12*, 1487.

12. Bouthegourd, E.; Rajisha, K. R.; Kalarical, N.; Saiter, J. M.; Thomas, S. *Mater. Lett.* **2011**, *65*, 3615.

13. Angellier, H.; Molina-Boisseau, S.; Dole, P.; Dufresne, A. *Biomacromolecules* **2006**, *7*, 531.

14. Yu, J.; Ai, F.; Dufresne, A.; Gao, S.; Huang, J.; Chang, P. R. *Macromol. Mater. Eng.* **2008**, *293*, 763.

15. Lin, N.; Yu, J.; Chang, P. R.; Li, J.; Huang, J. *Polym. Compos.* **2011**, *32*, 472.

16. Chen, G.; Wei, M.; Chen, J.; Huang, J.; Dufresne, A.; Chang, P. R. *Polymer* **2008**, *49*, 1860.

17. Zou, J.; Zhang, F.; Huang, J.; Chang, P. R.; Su, Z.; Yu, J. *Carbohydr. Polym.* **2011**, *85*, 824.

18. Duan, B.; Sun, P.; Wang, X.; Yang, C. *Starch/Stärke* **2011**, *63*, 528.

19. Song, S.; Wang, C.; Pan, Z.; Wang, X. *J. Appl. Polym. Sci.* **2008**, *107*, 418.

20. Mohammad, M. F.; Adeeb, S. E.; Mohammad, E. O. *J. Polym. Res.* **2003**, *10*, 119.

21. Han, J. A.; BeMiller, J. N. *Carbohydr. Polym.* **2006**, *64*, 158.

22. Funke, U.; Lndihaer, M. G. *Starch/Stärke* **2001**, *53*, 547.

23. Cho, C.G.; Lee, K. *Carbohydr. Polym.* **2002**, *48*, 125.

24. Meltem, C. *J. Polym. Res.* **2006**, *13*, 427.

25. Samaha, S. H.; Nasr, H. E.; Hebeish, A. *J. Polym. Res.* **2005**, *12*, 343.

26. Gidley, M. J.; Bupin, P. V. *Carbohyd. Res.* **1987**, *161*, 291.