

Photoinitiated Emulsion Graft Polymerization of Synthetic Monomers to Starch

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Abstract: Emulsion photopolymerization was used to graft synthetic monomers onto starch, an inexpensive, natural polymer. Effects of illumination method, photoinitiator, and monomer on reaction and properties were investigated. Improved grafting efficiencies were seen when starch, water, and photoinitiator were pre-illuminated. Chemical and physical properties of the grafted copolymer were obtained by gravimetric analysis and SEM. These results are useful for determining possible applications of polymer-g-starch copolymers in the paper and consumables industry.

Introduction

Starch-g-copolymers are of considerable interest to the paper industry. They provide a more robust starch for paper processing with improved dispersion properties. Traditionally starch-g-copolymers such as polystyrene grafted to starch are synthesized using high temperatures and pressures, thermal redox initiators, or γ -radiation.^{1,2,3,4,5} These methods require harsh conditions that may denature the starch, making processing difficult, and producing copious amounts of homopolymer. Recently, the grafting of styrene by thermal initiation in an emulsion system was attempted with marked success.⁶ In a system such as this, the highest concentration of monomer is sequestered in micelles, which helps decrease homopolymerization. The disadvantage of this method is the use of thermal initiation, which is inefficient and requires the reaction to be heated for long periods of time. Therefore, alternative initiation methods are of great interest.

Grafting of polymer to substrates via ultraviolet light has received more attention over the last two decades.^{7,8,9,10} Fouassier and coworkers have shown the most promising results by synthesizing graft copolymers of starch in homogeneous and heterogeneous mixtures of starch, monomer (hydrophobic and hydrophilic), and photoinitiator. Norrish Type I and Type II photoinitiators were used and achieved various grafting results. Variables such as irradiation time, irradiation wavelength, initiator concentration, monomer concentration, temperature of irradiation, and oxygen concentration all were critical in determining final grafting efficiencies.⁸ Starch-g-copolymers were formed with moderate grafting efficiencies but also produced large amounts of homopolymer. Therefore, methods which can separate initiation from the polymerization process and grafting process are needed to create graft copolymers with high grafting efficiencies.

The use of photopolymerization and emulsions together could decouple initiation from polymerization, allowing large amounts of graft polymer to be formed while decreasing the amount of homopolymer. Photopolymerization allows initiation to occur independent of temperature. Emulsion polymerization segregates high concentrations of monomer from the initiating system, which is a water-

soluble photoinitiator. This allows for efficient initiation in the continuous phase after which growing polymer particles can move into the micelles and continue polymerization. Figure 1 shows the basic grafting scheme used in this research, which unites these processes to create graft copolymers with higher grafting efficiencies and lower amounts of homopolymer.

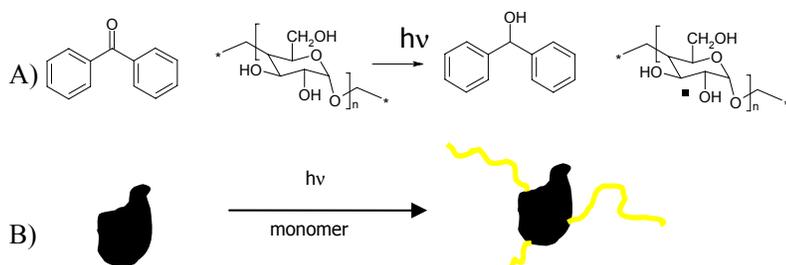


Figure 1. (A) Formation of radical on starch particle using benzophenone. (B) Formation of starch-g-polymer.

Experimental

In these studies, the synthetic monomers styrene (ST) and butyl acrylate (BA) (Aldrich Chemical Company) were grafted onto the starch amylopectin (STC, TCI Chemical Company). The surfactant sodium dodecylbenzene sulfate (SDBS, TCI Chemical Company) was used to make emulsions in Optima water (Fisher Chemical Company). Uvinul[®] 3048 (U3, BASF), a benzophenone derivative, was used to photoinitiate the graft copolymerization. All chemicals were used as received, except the starch, which was dried overnight in a vacuum oven at 60°C with desiccant present. Emulsions were prepared from these components using two basic formulations. The styrene emulsion formulations contained 14.5wt% ST, 14.5wt% STC, 0.7wt% SDBS, 0.1wt% U3, and 70.0wt% water. The butyl acrylate emulsions contained 14.0wt% BA, 7.0wt% STC, 0.8wt% SDBS, 0.2wt% U3, and 77.8wt% water.

Two illumination schemes were investigated to optimize grafting onto starch. In simultaneous-illumination experiments, the surfactant, water, monomer, starch, and initiator were mixed and stirred magnetically. The system was purged with N_2 for 20 min and then illuminated through a quartz window for a set period of time. In pre-illumination experiments, the starch, water, and initiator were mixed in the reaction vessel as shown in Figure 2. The monomer, surfactant, and water were placed in an addition funnel, which is shielded from the light source, and the system was purged for 20 min. After 20 min, the reaction vessel was illuminated for a specified time, and then the other components were added to the reaction vessel and reacted for 24 hrs. Each experimental setup was illuminated with a 200-W mercury-xenon arc lamp (Oriental Scientific), which has an intensity of approximately 60 mW/cm² at the quartz window surface.

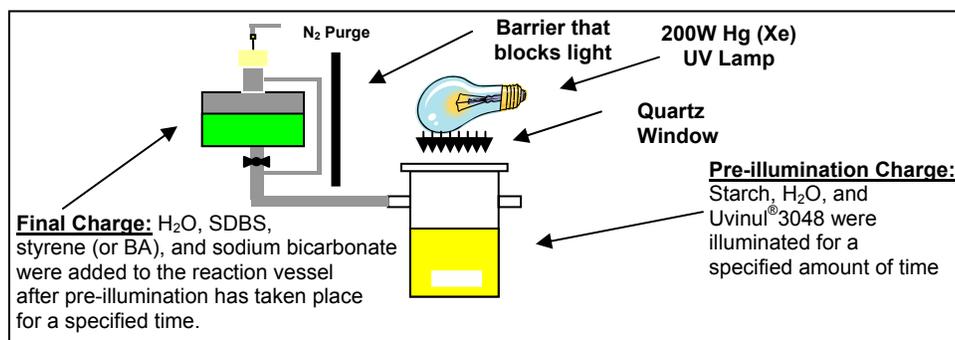


Figure 2. Illumination strategies for grafting of synthetic monomers to starch.

After the reactions were completed, the contents were precipitated in cold methanol and then filtered to remove homopolymer, starch-g-copolymer, and starch from the solution. These components were then dried in a vacuum oven overnight at 60°C. The reactions were characterized gravimetrically to determine percent yield (% yield), which is shown in Equation 1⁶.

$$\% \text{ Yield} = \frac{\text{Mass of Monomer Polymerized}}{\text{Initial Mass of Monomer}} \times 100 \quad (1)$$

After % yield was determined, approximately 2 g of the mixture was placed in a moderately sized Soxhlet extractor, and the homopolymer was removed from the sample. The sample was then massed, and grafting efficiency was calculated using Equation 2⁶.

$$\text{Grafting Efficiency (GE)} = \frac{\text{Mass of Grafted Polymer}}{\text{Mass of Homopolymer} + \text{Mass of Grafted Polymer}} \times 100 \quad (2)$$

Scanning electron micrographs were also taken of the samples to enable qualitative comparisons of the surface textures. The surface of unmodified starch was compared to that of the simultaneously illuminated and pre-illuminated samples with a magnification of 2000× after coating them in gold for analysis.

Results and Discussion

Simultaneous-illumination Experiments

In simultaneous-illumination experiments, all chemical species were present at the time of initiation. The effect of this illumination scheme upon the grafting results is shown in Table 1 for both emulsion formulations.

Table 1. Grafting results from simultaneously illuminated ST and BA emulsion systems.

Monomer	% Yield	Grafting Efficiency
Styrene	50%	≈0%
Butyl acrylate	87.8%	11.5

When simultaneous illumination is carried out, active centers can be formed at many different sites. For instance, U3 may abstract hydrogen from surfactant or monomer, creating sites for homopolymerization to occur. This is reflected in the data from Table 1. Very little grafting occurs under these conditions, although a large amount of homopolymer is produced. Therefore, an alternative method is required that will allow the formation of the radical to predominantly occur on the starch particles initially.

Pre-illumination Experiments

In pre-illumination experiments, the starch and photoinitiator were illuminated prior to the addition of the monomer and surfactant. This allows for the free-radical center to form on the starch particle before it can form elsewhere. The effect of increasing the pre-illumination time upon the grafting results is shown in Table 2 for both emulsion formulations.

Table 2. Grafting results from pre-illuminated styrene and butyl acrylate emulsion systems.

Starch-g-PS			Starch-g-PBA		
Pre-illumination Time	% Yield (%)	GE (%)	Pre-illumination Time	% Yield	GE (%)
0	50.0	0	0	87.8	11.5
5	37.5	12.5	2	89.1	35.9
10	39.5	7.9	5	67.5	60.2
20	38.4	11.5	12	86.1	77.7
			20	87.5	81.4

The simultaneous illumination of styrene emulsion systems yields little, if any grafting; however, after just 5 min of pre-illumination, the grafting efficiency increased to 12.5%, although the percent yield decreased by about 12%. Further increase of the pre-illumination time does not result in a significant change of grafting efficiency.

These results were also confirmed for styrene in the SEM micrographs of starch before and after modification, shown in Figure 3. The unmodified starch is smooth in texture and rounded. The starch-g-PS sample that was synthesized by simultaneous illumination has some protrusions and is rougher in texture than the unmodified starch. The pre-illuminated starch-g-PS sample has even more protrusions than the simultaneously illuminated sample. This qualitatively indicates that pre-illumination does indeed create polymers with higher grafting efficiencies than simultaneous illumination.

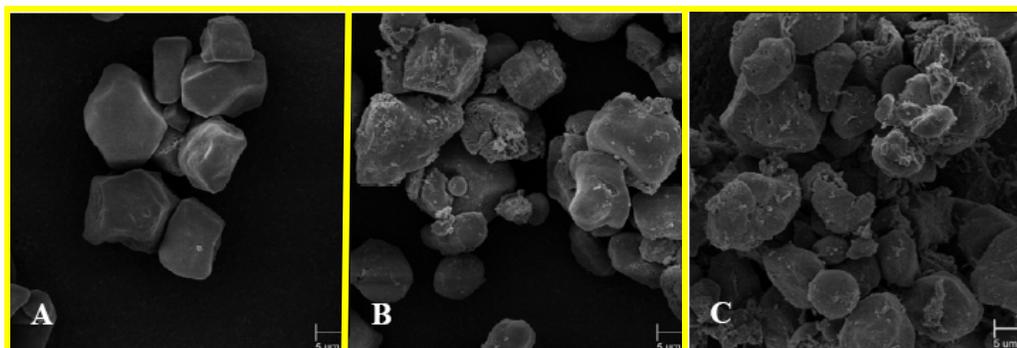


Figure 3. SEM micrographs of unmodified starch (A), simultaneously illuminated starch-g-PS (B), and 15-min pre-illuminated starch-g-PS (C).

In the pre-illuminated starch-g-PBA system, pre-illumination of 2 min results in a grafting efficiency of 36%. If the pre-illumination time is increased to 5 min, the grafting percent almost doubles to 60%. If the pre-illumination time is increased further, higher grafting efficiencies are obtained. Unlike the styrene system, the % yield remains constant and does not show dependence on pre-illumination time. The 5-min pre-illumination experiment is an exception; however, this deviation may have been due to film formation on the quartz window or a decrease in light intensity due to improper placement of the light during that particular run.

Pre-illumination is more effective in these systems than simultaneous illumination. During pre-illumination, free-radical centers form on the starch particles before they can form elsewhere, increasing the likelihood that monomer will add to these active centers. If the components are mixed together and simultaneously illuminated, there is a much higher probability that the monomer will self-initiate, thereby creating large amounts of homopolymer.

The butyl acrylate samples were affected more significantly by pre-illumination than the styrene samples. This could be a kinetics effect in which the faster polymerizing molecules graft more efficiently to the starch radical and form less homopolymer in the process. This indicates that starch radicals may be longer lived in the BA system and that ST may quench radicals, thereby preventing higher grafting efficiencies at increased pre-illumination times. These phenomena will be studied using electron spin resonance spectroscopy in the future. Another variable that may influence the calculation of grafting efficiency values is the method of homopolymer extraction. Soxhlet extraction slowly removes homopolymer from these samples. Polyacrylates tend to swell when mixed with good solvents, such as chloroform. When this occurs, they create a stagnant pool of polymer and solvent, and the polymer grafted to starch will eventually clog the Soxhlet extractor thimble. Therefore, grafting efficiencies higher than they actually are may be calculated. Alternative methods are being developed to remove the homopolymer more efficiently and more accurately.

Conclusions

The grafting of polymers, such as polystyrene and poly(butyl acrylate), onto starch was accomplished by photopolymerization in an emulsion system. Two illumination strategies were investigated to improve grafting efficiency in these systems. Pre-illumination of the starch and photoinitiator proved to be much more effective than simultaneous illumination of the entire emulsion formulations. Depending on the length of pre-illumination, grafting efficiencies were increased by 10% for starch-g-PS samples and by over 80% for starch-g-PBA. This emulsion photopolymerization technique continues to hold much promise as a more efficient and environmentally friendly method to produce starch-g-copolymers for use in the coatings, composite plastics, and recycled paper industries.

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References

1. Fanta, G.F., Burr, R.C., Russel, C. R., and Rist, C. E.: Amer. Chem. Soc. Abstr. Papers 23 (1965), 149.
2. Fanta, G. F.; J. Appl. Polym. Sci. 10 (1966), 929.
3. Retes, Z., Rist, C. E., and Russel, C.R.: J. Polym. Sci. A1, 4, (1966).
4. Fanta, G. F.: J. Appl. Polym. Sci. 22 (1978), 2991.
5. Mehrotra, R., and B. Ranby; J. Appl. Polym. Sci. 22 (1978), 2991.
6. Cho, Chang. G., Lee, K. Carbohydrate Polymers, 48, 125, (2002).
7. Herold, R., Fouassier, J. Die Angewandte Makromolekulare Chemie. 86, 109, (1980).
8. Herold, R., Fouassier, J. Starch. 33, 90, (1981).
9. Ma, H., Davis, R. H. Bowman C. N., Macromolecules. 33, 331, (2000).
10. Yang, W., Rånby, B. J. Appl. Polym. Sci., 62, 533, (1996).