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Starch Grafted With Polyacrylic ACID as A Renewable Alter-Native for Fossil Based Performance Polymers.

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Abstract: Graft copolymerization of acrylic acid onto starch can provide renewable alternatives for current applications of water soluble performance polymers from fossil resources. In our laboratory, Fenton's reagent was mostly used as the initiator for graft copolymerization experiments, in aqueous solutions. A major challenge with the homogeneous system is the selectivity of grafting versus homopolymer formation. Important factors that determine the grafting selectivity are discussed, and methods to improve it are proposed. In a batch process, adding monomer in portions over time proved sucessful. This provides a principal breakthrough of the trade-off between grafting percentage and graft selectivity that is characteristic for grafting with hydrophilic monomers. .

Keywords: Starch graft copolymerization; selectivity of the grafting reaction; water solubility of the monomer as a key factor; methods to improve selectivity with water soluble monomers and indirect initiation.

1. Introduction

To meet the rapidly growing demand for materials made from renewable resources, biopolymers like starch are an interesting option. There is a vast array of polymers that are now still mostly synthesized from fossil resources, which can or may be replaced by materials based on carbohydrates. Starch is readily available from many botanical sources like corn, potatoes, cassava and more, and as yet relatively inexpensive. However, native starches need chemical modifications to turn the long molecules into competitive alternatives for a class of polymers that is called 'performance' polymers. Examples of such polymers are superabsorbent networks or hydrogels, thickening agents, flocculation agents, textile sizing materials and detergent co-builders. Each of these possible applications has its own demands on the properties and structure of the molecules, which is discussed in detail in a previous paper (1). The key factor of starch modification is to add functionalities that are not present in native starch. An important method to impart these and to add new properties, is to attach chains of functional polymers to the starch backbone by graft copolymerization. The most usual method to synthesize such a material is by free radical add-on polymerization with vinyl monomers [2,3]. In our laboratory, acrylic acid has been the monomer of choice since composite polymers of starch with side chains of polyacrylic acid are a promising candidate to replace many of the current water-soluble performance polymers based on petrochemicals. Fenton's reagent in was used as the initiator for experimental polymerization runs in the aqeuous phase with acrylic acid and gelatinized starch. The Fenton's ingredients ferrous ammonum sulfate and hydrogen peroxide are cheap and the reactions can be operated at ambient conditions, which would be advantageous for future scaling up of the process [4]. The use of starch as a basis for new polymers also holds the promise of better long-term biodegradability of the products.

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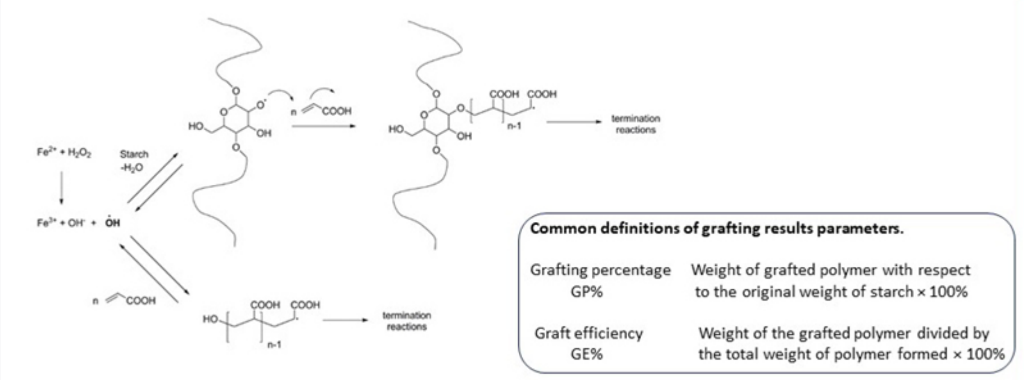
In this short paper, the focus is on graft selectivity, which should be good to prevent the formation of homopolymer acrylic acid as much as possible. In the homogeneous system with Fenton's initiator and the water-soluble monomer acrylic acid it is more challenging however to get a good graft selectivity, as compared to grafting reactions with hydrophobic monomers or with a different type of initiator. The reasons behind these differences will be discussed, and then methods to improve the selectivity of the grafting reaction, mostly based on our own laboratory results, are presented.

2. Graft copolymerization reactions and the question of grafting selectivity

The scheme of Figure 1 shows the important reaction steps. From this scheme, it is obvious that reactions towards homopolymer are intrinsic to the type of starch activation via radicals produced in the solution, as is the case with Fenton's reagent. How many of the OH radicals react with starch or with monomer is a matter of chance and probability. This is dependent on various reaction conditions and thus can be influenced, as will be discussed further on. The result of the grafting process is usually expressed with the parameters GP and GP also shown in Figure 1.



Common definitions of grafting results parameters.	
Grafting percentage GP%	Weight of grafted polymer with respect to the original weight of starch × 100%
Graft efficiency GE%	Weight of the grafted polymer divided by the total weight of polymer formed × 100%

Figure 1. Schematic representation of the reactions involved in the grafting of acrylic acid from gelatinized starch as a backbone with Fenton's initiator. The upper section is the desired grafting reaction, the lower section represents the less wanted homopolymer formation.

The parameter GE represents the selectivity of the grafting reaction, at the end of the polymerization process or the 'final' selectivity. Cross-terminations, which occur when a growing grafted polymer chain would terminate with a homopolymer chain, can contribute to the overall (final) selectivity. However, the most important factor will be the ratio between radicals that activate starch or activate monomer, which is the selectivity at the moment of initiation. We can identify a number of reaction parameters and factors that have major influence on graft selectivity. However, since in literature the progress of graft selectivity during the reaction is hardly ever reported, the effect of reaction parameters must be derived from 'final' selectivity data. The presence of homopolymer in the product may require a difficult and probably uneconomic separation after the reaction. However, for some potentials applications the presence of some homopolymer may be tolerated, as discussed in more detail in [1]. Still, the general desire for good graft selectivity remains.

3. Important factors for the graft selectivity

Factor 1: the choice of the initiator

The activation by creation of radicals on the starch backbone is logically most selective if an initiator is used that has a direct reaction with starch. This, at least in theory, avoids the influence of the chance to activate monomer, a chance that is always present when the radicals are created at random in the solution. Examples of initiators that create radicals in the solution are not only Fenton's reagent but also persulfates (ammonium-, potassium-) and peroxides (butyl, benzoyl). For more selective direct activation, Cerium

Ammonium Nitrate (CAN) is used in many grafting systems as reported in literature [2,3,5], although the expected great selectivity is not always obtained . There are some more relative disadvantages associated with CAN as the initiator. Cerium is expensive and both initiator efficiency and the reaction rate with this system are relatively low. Therefore, in our opinion this initiator is more suited for laboratory scale studies than for larger scale applications.

Apart from chemical initiation, there are also several publications on the use of high energy or magnetron radiation to start the grafting reaction [2,3,6]. However, high energy radiation requires large and expensive equipment. A common issue with all irradiation activation methods is that the penetration depth of the radiation energy into a starch solution will be small which could make it difficult to apply irradiation initiation in larger tank- or tube reactors.

For these reasons, in the present paper we focus on the chemical initiation methods that create radicals in the solution like the Fenton's reagent which was mostly used in our laboratory work.

Factor 2: reaction variables

It is evident that several reaction variables will have a large influence on the graft performance and selectivity. Both initiator concentration and reaction temperature usually show an optimum value, in GE and in GP, [2,5,7] according to the following. At low initiator concentration and/or temperature, there may just not be enough radicals created to start a substantial number of grafted chains. Higher initiator dosage and increased temperature means more radicals, but at a certain point there will be an excess of free radicals that give rise to early terminations (in other polymerizations known as 'dead end reactions'), so grafting results go down.

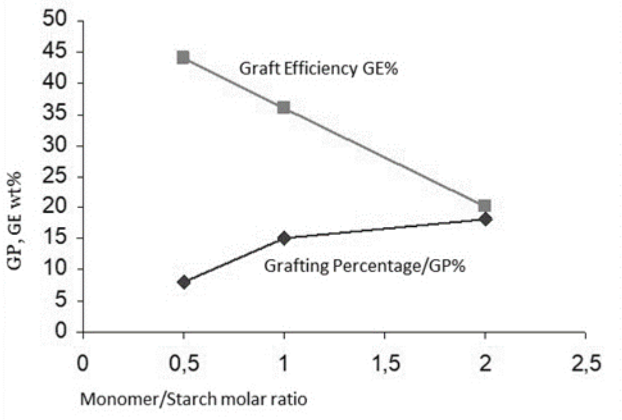


Figure 2. Opposite trend in GP and GE at increasing M/S ratio.

The relative concentrations of monomer and starch, the M/S molar ratio, is another important factor. With Fenton's initiator we have seen an opposite effect of the M/S ratio, which is shown in Figure 2 [4]. Such an effect is reported in other literature sources as well, e.g. [7,8]. At higher dosage of monomer, there can be more and longer grafts, hence a higher GP. But with lots of monomer in the system, there is also a higher chance that monomer molecules get activated towards homopolymerization. This means that the ratio of monomer to starch must be low to achieve good GE – but this will be at the cost of a lower amount of functional new polymer groups. So, the optimal value here will be a trade-off.

Factor 3: water solubility of the monomer.

Most grafting research with starch has been done with water as the main solvent. However, the impact of the factor water solubility of the monomer is almost never addressed in literature, probably because most researchers work with one single monomer. In the graft copolymerization of methyl methacrylate, graft selectivity results in the order of 90% or better are reported, e.g. in [3, 6, 9]. Also, with acrylonitrile [3,10] or styrene [11], comparable good graft selectivity has been reported. The common factor between these monomers is that they are poorly water soluble, up to hydrophobic. Those selectivity results are in sharp contrast to results for acrylamide and acrylic acid monomers, where GE is usually lower, even in the order of only 20-30% [2,4,10,12]. These reagents are water soluble and hydrophilic.

In an aqueous reaction environment, hydrophobic molecules will stick together and form droplets, which gives rise to a separate discrete phase. In some cases, it is even the rate of mass transfer through the interface which determines the overall reaction rate [11,13]. With the monomer in a separate phase, concentration of monomer molecules in the continuous phase with the initiator and (gelatinized) starch is always low. From data like those in Fig.2 it is evident that this situation is favorable for high graft selectivity. In systems with hydrophilic monomer however, monomer is all around in the aqueous phase and hence has more chance to be activated for a reaction to form homopolymer.

For this reason, grafting reaction systems with hydrophilic monomer like acrylic acid pose the greatest challenge with respect to obtaining sufficient graft selectivity.

3. Methods to improve the graft selectivity

Several methods and ideas have been tested in our laboratory, with mixed success.

Use of a polymerization crosslinker

When a network of polymer is needed, like in the synthesis of superabsorbents, a polymerization crosslinker is usually added to the reaction system. N, N′-methylene bisacrylamide (MBAM) is the most common reagent and was also used in our laboratory [4,14]. When during the reaction one of the two vinylic (C=C) functions has become incorporated in a growing grafted chain, the other can connect to a homopolymer chain. So, at least in theory, this may increase the amount of polymer attached to the backbone starch hence give a higher graft selectivity. In [14] is seen that indeed GP and GE can be increased this way, but more experimental proof would be needed. Of course, this way of improving the final selectivity can only apply to systems where a crosslinker is used.

Pre-initiation, starch activation before adding monomer.

In literature, there are examples that starch activation before the monomer is added to the system leads to excellent graft selectivity, e.g. [3,8]. With Fenton’s reagent however pre-initiation gave disappointing results because the starch was rapidly degraded to small fragments, which showed up as a sharp decline of the viscosity of the gel [8], This method is therefore considered unsuitable for our grafting reaction system.

Dedicated dosage, adding the monomer in portions over time in a batch process.

The principle of dedicated dosage is most easily explained with the ‘artist impression’ in Figure 3. The required amount of monomer is not added before the initiator is added, which defines the start of the polymerization reactions, but divided over several smaller portions at time intervals. For exploratory experiments, the monomer was divided over five portions of equal amount. The first portion was added before entering the initiator, the others in five-minute intervals. This resulted in improved graft selectivity together with a higher grafting percentage. Compared to the ‘conventional’ reaction method, an increase of GP from 18% to 28% was obtained, along with an improved graft selectivity (GE) of 20% until 31%. These exploratory experiments were presented at ECCE-10 [15] and after that the results have been confirmed by several more and duplicate experiments. Although the GE% is not yet in the range seen for grafting of hydrophobic monomers, at least it has been demonstrated that this method can break the trade-off between GP and GE as shown in Fig.2. The results may get even better by refining the method, which is a lead for future research work.

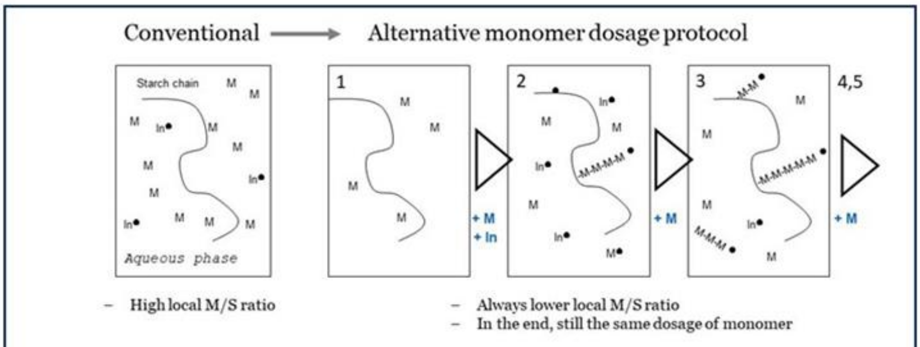


Fig. 3. The principle of dedicated dosage versus all monomer at the start of the reaction

3. Conclusions

The mechanism that causes large differences between the selectivity of grafting hydrophobic versus hydrophilic monomers onto starch has been elucidated. It is clear that copolymerization of acrylic acid with indirect initiation poses the greatest challenge, since with increased monomer concentration, grafting percentage and selectivity show an opposite trend. A method of dedicated monomer dosage, in portions over time, has shown potential to improve both GP and GE. This can be considered a principal breakthrough, which still needs further refinement. Also, the implementation of such a method in a continuous reactor is a further R&D challenge.

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