

Special Article – Polymers

Chemical vs Microwave Initiated Tragacanth Gum Graft Copolymers: a Real Perception

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Synthesis of smart hydrogels is gaining enormous interest in a large number of applications, such as bio immobilization and drug delivery. Graft polymerization is an interesting tool to develop graft copolymers. There are several ways to carry out grafting of a monomer into TG matrix where chemical or microwave irradiation have been widely investigated. Each of them has specific pros and cons towards the copolymer development but need to look at the real perception of grafting process. Microwave has a tendency to produce more of interpenetrating networks while chemical initiation leads to more of a regular graft copolymers. The concept is being explained in terms of the results obtained under the two approaches of graft copolymer preparation.

Keywords: Tragacanth gum; Itaconic acid; Graft copolymer; Microwave irradiation; Chemical initiation

Introduction

Biopolymers have enormous potential in several technologically important domains such as superabsorbent, ion exchange materials, and scaffolds for tissue engineering [1]. However, designing of these polymers becomes very important to introduce newer features in the biopolymer matrix. Graft polymerization is the unique process to functionalize polymeric materials for various applications. The advantage of the grafting process is that the base polymer acquired additional characteristics without much affecting its inherent features. Grafting has been used as an interesting tool to functionalize biopolymers [2-4]. The extent of modification may be properly controlled by careful selection of the monomers. This way one can introduce carboxyl, amide, amino, sulfonic and hydroxyl groups in a virtually any polymer irrespective of its chemical nature. This is how acrylic acid has been widely used to develop biopolymer hydrogels with carboxyl functionality [2]. Among different approaches, the chemical and more recently the microwave irradiation have been extensively studied. The control over degree of grafting can be achieved by variations in the monomer concentration, reaction temperature, initiator concentration and the reaction medium. This leads to the copolymer structure which has a wide range of swelling, ion exchange capacity and the drug encapsulation and release pattern.

The nature of the grafting process would therefore lead to the creation of different structures which may be reflected in the variation of the properties and the performance of the graft copolymers. In this report, we have looked at the physico-chemical aspects of the graft copolymers prepared by chemical and the microwave irradiation based on the Tragacanth gum-itaconic acid system.

Experimental

The graft polymerization of itaconic acid on Tragacanth Gum (TG) was carried out using two different approaches. The mixture of TG and itaconic acid in aqueous system was exposed to microwave radiation as reported earlier [3]. The chemical initiated grafting was

carried out by using Potassium Persulfate (KPS) as the initiator under nitrogen atmosphere [4]. The details of these experiments have been discussed in these two publications.

Results & Discussion

We have been working on the graft polymerization of the itaconic acid on tragacanth gum using Microwave Radiation (MGTG) as well as by Chemical Initiation (CGTG) processes [3-5]. We have observed that in spite of the similar components, the physico-chemical behavior of the grafted hydrogels prepared by these two routes is significantly different from each other. These variations are in the form of the smartness in pH-dependent delivery of the bioactive components (Table 1). The changes in physico-chemical structure may arise only if the two processes lead to different structures of the grafted matrix. It is important to understand these structural changes are process-dependent and are reflected in their properties.

The important feature is that the microwave irradiation is achieved under open air atmosphere and hence the whole process takes place by thermal breakage of the bonds and radical generation (Figure 1). It is very difficult to trap these radicals by monomers due to the presence and scavenging nature of the oxygen around these radicals. Such a scenario may lead to the nonspecificity in the grafting process. The chemical grafting, on the other hand, is carried out under inert atmosphere so that the radical scavenging by oxygen is negligible (Figure 1). The radicals generated by initiator are therefore involved in the polymerization of the monomer and more specifically in the grafting process.

It seems that the microwave grafting doesn't show a real perception of the smart material. The drug (Ampicillin) release in the microwave assisted grafting shows hardly any appreciable variation with the change in the pH range of 2.2-9.4. On the other hand, the grafting using potassium persulfate shows strong dependence on the pH of the medium. The swelling as well as the drug release vary with the pH of the medium. The rate of drug release was observed

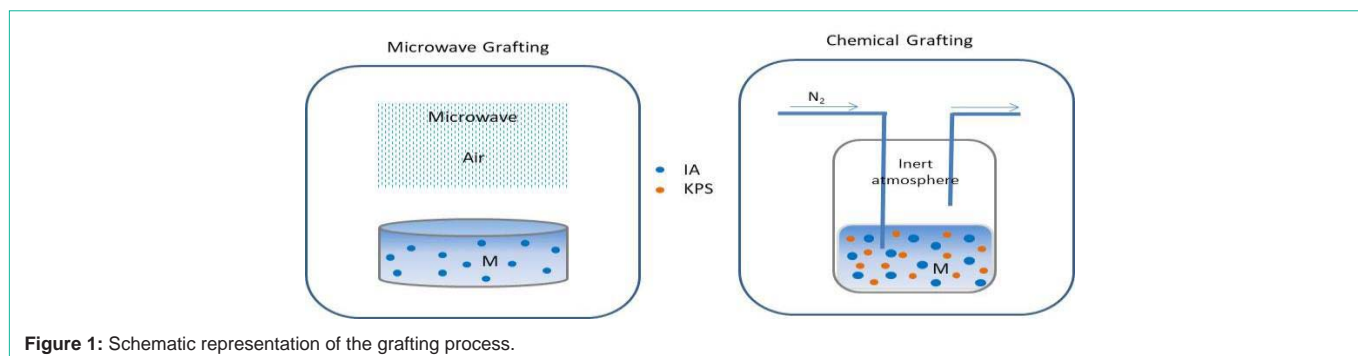


Figure 1: Schematic representation of the grafting process.

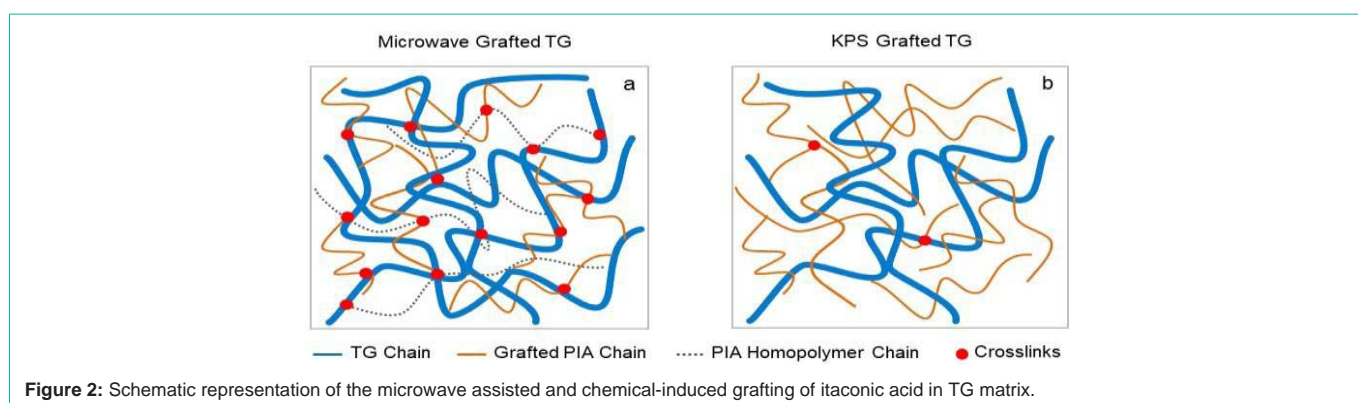


Figure 2: Schematic representation of the microwave assisted and chemical-induced grafting of itaconic acid in TG matrix.

Table 1: Comparison of the microwave and chemical-induced grafting process.

Features	MG TG ³	CG TG ⁴
Process	Irradiation in open air	Initiation under inert conditions
Homopolymer Separation	Not accomplished	Accomplished
Drug Release Rate	No appreciable difference at different pH	at pH 2.5: 21%/h at pH 7.4: 41%/h

to be almost twice at 7.4 pH as compared to the 2.5 pH (Table 1). It seems that the structure developed by chemical grafting leads to the grafted chains in such a way that they exhibit independent nature as Polyitaconic Acid (PIA) chains. However, this is not the scenario when microwave grafting is carried out. The chain mobility and their independent identity is significantly marred by interlinking of chains.

We propose a model which can help in understanding real perception and the mechanism of the grafting in these two systems (Figure 2). In microwave assisted grafting, both the biopolymer and hydrogel are exposed to the radiation. The monomer, therefore, may form homopolymer along with the grafted branches during the polymerization. As the irradiation progresses, it is not only the exposure of the monomer, but also the grafted matrix and the PIA homopolymer is irradiated and forms intermolecular crosslinking of the grafted chains together with the biopolymer matrix leading to a structure similar to the Interpenetrating Network (IPN) as represented in (Figure 2a). This leads to the formation of a network structure where grafted and homopolymer both become an integral

part of the main structure. The red circles in the Figure 1 show the crosslinks within the hydrogel matrix. Under such a scenario, PIA chains lose their independent nature and do not show pH-sensitivity due to the strong restrictions on their mobility. The chemical grafting, on the other hand, leads to very well defined structure where the grafting and homopolymer formation proceed simultaneously, but the homopolymer does not undergo any network formation and is separated out by treating with water. Even if any crosslink is formed during the grafting, it may be negligible and does not interfere with the smart nature of the hydrogel as represented in (Figure 2b). The grafted matrix, on the other hand, remains intact and exhibits pH-sensitivity. The hydrogel prepared by the chemical approach, therefore, exhibits true smartness and shows pH-dependent drug release in a system.

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